
Chapter 3

Blended Cement

BLENDED CEMENT

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1. INTRODUCTION

A blended cement is a binder that contains - in addition to Portland cement clinker and calcium sulfate - one or more of the following materials:

- ◆ a latent hydraulic material (granulated blast-furnace slag)
- ◆ a pozzolanic component (natural pozzolana, fly ash, silica fume, burnt clay, a.s.o.)
- ◆ a filler (usually limestone).

1.1 Latent Hydraulic Materials

Latent hydraulic materials have a natural hydraulic potential (i.e. they can develop silicate hydrates by hydration reactions), but require an activator such as:

- ◆ Lime
- ◆ Portland cement clinker
- ◆ Gypsum
- ◆ Chemical activator

in order to accelerate the reaction with water. Blast-furnace slag is the most typical latent hydraulic material.

1.2 Pozzolanic Materials

They can give rise to the formation of silicate hydrates only in presence of lime (calcium hydroxide, Ca(OH)_2), as a consequence of its reaction with the amorphous (glassy) silica contained in the pozzolana. The hydration reaction of Portland cement clinker with water will provide the necessary lime to make the pozzolanic reaction happen.

Natural pozzolanas, generally of volcanic origin, and low-calcium fly ashes are the most commonly used materials belonging to this group.

1.3 Inert Additions (fillers)

Inert additions possess no hydraulic or pozzolanic activity, but contribute to cement properties other than strength development.

Limestone filler is the most commonly used, particularly in the production of fillerized cements, with up to 35% clinker replacement, and in the manufacture of masonry cements (up to 75% limestone).

1.4 Alternative terminology

Depending on the idioms of the place of use, the reference standards and the materials involved, blended cements can be also named differently, e.g.

- * composite cements
- * fillerized cements
- * slag cements
- * pozzolanic cements, a.s.o.

The materials, besides clinker and gypsum, used as constituents for blended cements can also be named, according to the nature and performance in cement, as

- * mineral components
- * mineral additions
- * mineral additives
- * mineral admixtures
- * fillers
- * cement extenders.

2. SIGNIFICANCE OF BLENDED CEMENTS

The principal reason for the production of blended cements is economic and environmental, although in most cases blended cements perform better than Portland cement.

Blended cements allow an economy of fuel and an increase of cement production due to the lower clinker/cement factor. During the last thirty years, a significant increase in the use of alternative materials in the manufacture of blended cements, or as additions in concrete, has been recorded owing to unquestionable technical advantages, such as:

- * improved durability (beneficial for service life of concrete structures)
- * reduced heat of hydration (beneficial for casting of thick sections)
- * reduced alkali level of the blend (to minimize the risk of alkali-silica reaction)
- * improved characteristics of fresh concrete.

Possible disadvantages, such as

- * slower rates of strength gain at early ages (and at lower temperatures)
- * higher sensitivity to poor curing

are largely overcome by the advantages gained in the overall performance.

Production of blended cements, then, has effect on the

- ◆ reduction and optimization of production costs by
 - improved clinker factor
 - saving on thermal and electrical costs
 - increased cement output,
- ◆ activities related to environment protection and preservation by
 - conservation of natural fuels and mineral resources
 - use of by-products as mineral components
 - reduction of CO₂ and heat emission,
- ◆ differentiation of products and applications by
 - opportunity to produce tailored products
 - improvement of cement properties for special applications
 - fulfillment of durability issues in concrete construction.

2.1 History

Slags have been known since ancient civilizations. It has been illustrated that ancient Egyptians produced glass slags, rich in vesicles (air bubbles) and containing crystals of the minerals melilite and tridimite, by burning wheat straw. This contains opal, an amorphous form of silica, that combines during burning with alkali to form glassy slag.

More than 2000 years ago, the Romans discovered the activity of the volcanic ash from Pozzuoli when it was mixed with lime. This was used in many structures that lasted through the centuries and are still existing today, such as aqueducts, bridges, historical buildings. Vitruve, architect and engineer in the 1st century AC was the first who tried to explain the reactions that transform some rocks into cementitious materials.

More recently, the production of blended cements has been practiced for many decades in many countries. History of use of blast furnace slag (BFS) goes back more than 100 years when the iron and steel industries in England, Germany, Czechoslovakia, etc. operated their own cement factories. Cements with natural Pozzolanas as an addition have been firmly installed in the Italian and Greek markets for decades, and are used in practically all applications involving concrete construction.

2.2 Present situation

The observed growth of the production of composite cements in the recent years is roughly indicated in the following table 1:

Table 1 Production of Composite Cement in the World

Addition → Situation	Slag	Ash	Pozzolan	Limestone
established	EC countries Latin America East. Europe Japan South Africa	Europe Oceania South Africa	Italy Turkey Latin America Greece	Europe Morocco
increasing	Australia Brazil Canada India	Canada Far East	Middle East Far East	East. Europe New Zealand

3. OVERVIEW ON MINERAL COMPONENTS

3.1 Classification of mineral components

As already mentioned in the definitions, secondary constituents of a blended cement can be

- ♦ (latent) hydraulic materials
- ♦ pozzolanic materials
- ♦ inert materials (fillers)

The following Table 2 summarizes the types of constituents used in the production of blended cements.

Table 2 Constituents of Cement

1. Principal constituents	
. clinker	- various clinker types
. set regulator	- gypsum, anhydrite
	- gypsum by-products
	- limestone
2. Secondary constituents	
. hydraulic materials	- blast furnace slag
	- other by-product slag
. pozzolanic materials	- natural pozzolan
	- fly ash, bottom ash, silica fume
	- artificial pozzolan
. fillers	- limestone, marl, siliceous sand/ rock
	- kiln dust
3. Chemical additives	
	- grinding aids
	- quality improvers

3.2 Types of Mineral Components

Suitable materials for blended cement production can be natural or artificial. An artificial component is either derived from industrial production as a by-product, or can be obtained by thermal activation of natural materials or by-products.

The following Table 3 gives a concise overview of these materials.

Table 3 Different types of mineral components

SLAGS		POZZOLANAS	
artificial		natural	artificial
* granulated blast furnace slag		* volcanic ashes	* activated natural materials
* all other rapidly cooled slags		* tuffs	* activated industrial by-products
		* opaline cherts and shales	
		* diatomaceous earth	
		* rhyolites, etc.	
Activated natural materials		Activated industrial by-products	
- calcinated clays		- pulverized ashes of lignitic or anthracitic coal	
- calcinated volcanic rocks		- bottom ash	
- metakaolins		- industrial SiO ₂ rich residue (silica fume)	
- Kalsin		- calcinated red muds	
- calcinated shales		- calcinated wastes	
- etc.		- pulverized clay bricks or tiles	

3.3 Chemical Composition

- ♦ Although these materials have very different properties in many respects, they have one thing in common: they consist essentially of the same major chemical elements as PC clinker: **SiO₂ - Al₂O₃ - CaO**.

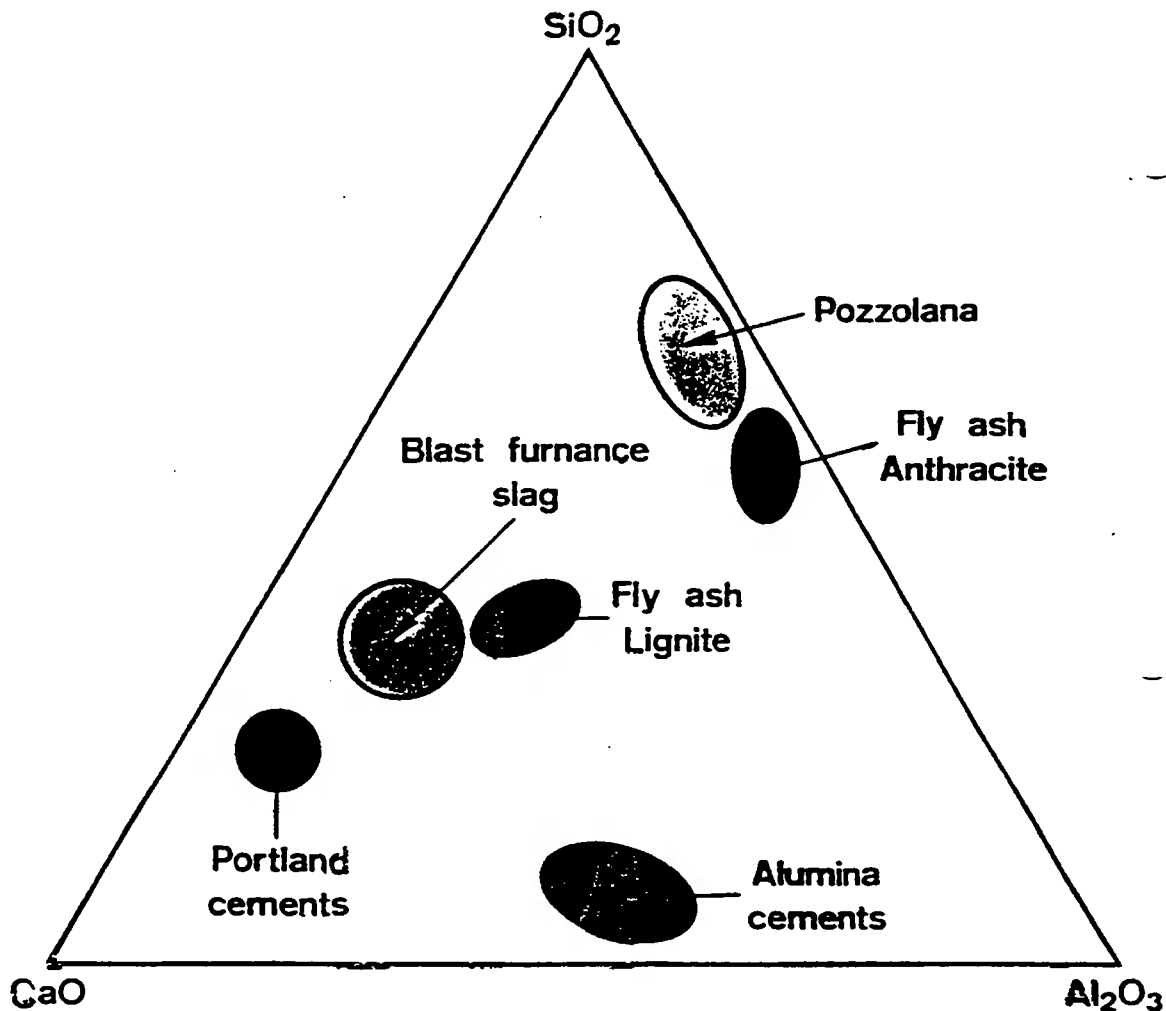
The respective proportions regarding the CaO - SiO₂ - Al₂O₃ diagram are shown in Table 4 and represented in Fig.1.

Table 4 Chemical Composition of Hydraulic Additions (on the basis of dried and calcinated materials)

Elements	Blast Furnace Slag	Natural and/or Artificial Pozzolan	Class F Fly Ash
SiO ₂	30 - 40	50 - 75	40 - 65
Al ₂ O ₃ (TiO ₂)	8 - 25	15 - 25	15 - 40
Fe ₂ O ₃	0.5 - 1.5	3 - 10	3 - 17
CaO	35 - 45	1 - 15	1 - 10
MgO	1 - 18	< 5	- 3
SO ₃	1.5 - 6	0.1 - 1.5	0.3 - 3
K ₂ O	0 - 0.5	0.5 - 4	2 - 3
Na ₂ O	0 - 0.5	0.5 - 4	0.4 - 2
MnO	0.2 - 2	-	< 0.3

Most slags, Pozzolanas and fly ash must be dried before utilization.

Fig. 1 CaO-SiO-AlO-System



3.4 Hydration Aspects

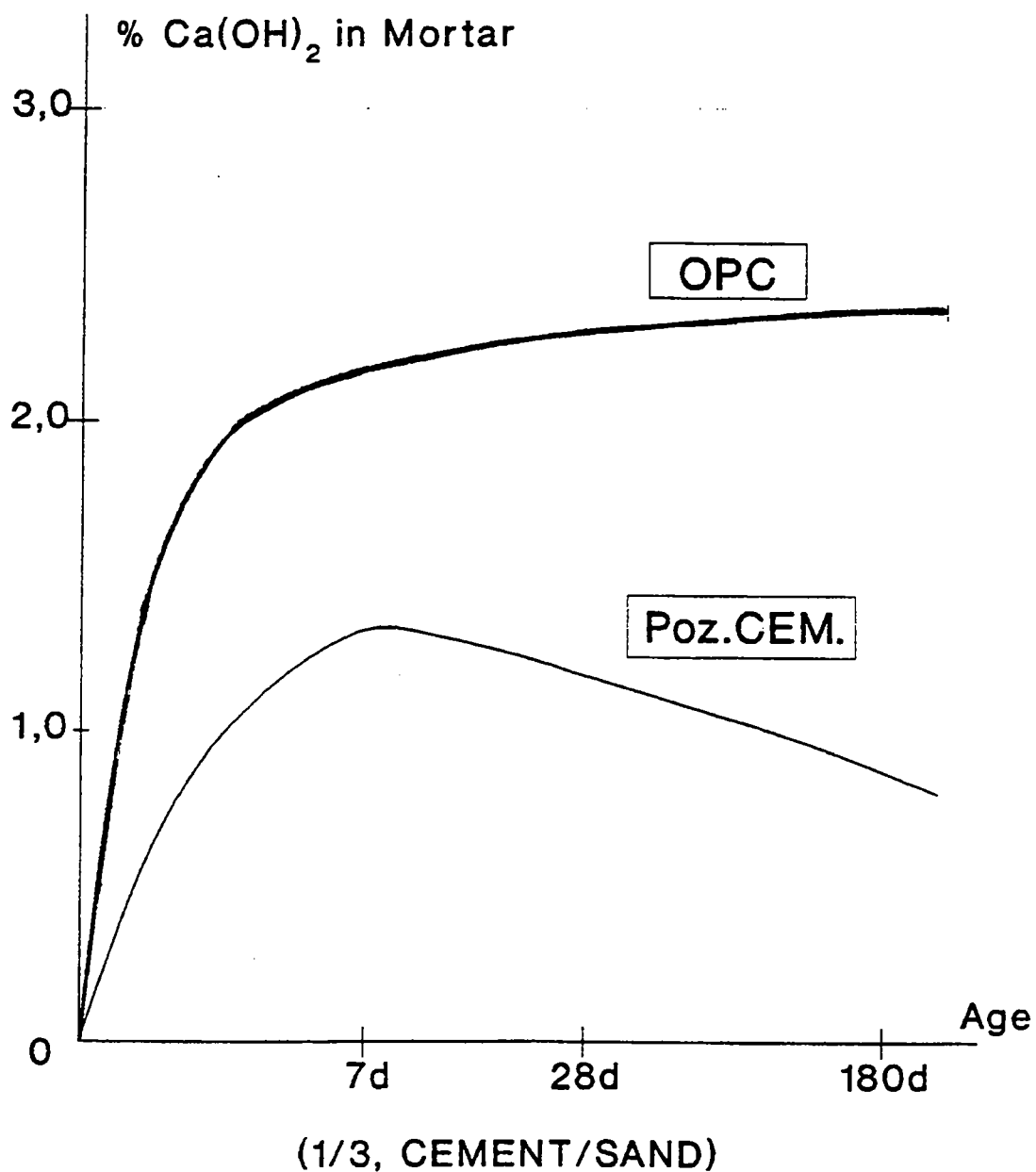
Both slag and pozzolan must be activated for adequate hardening.

Slag has a high silica and calcium oxide content. If activated by OH^- or SO_4^{2-} ions, it displays hydraulic activity (cementitious properties). In practice, the activation is realized by addition of lime, Portland cement clinker (OH^-) or gypsum (SO_4^{2-}).

Silica, and alumina at a lower degree, are the main components of pozzolan, whereas the calcium oxide is low. Pozzolan supplies the silica (or alumina) that reacts with added lime or with the lime (Portlandite) produced by hydration of Portland cement clinker.

When analyzing the calcium hydroxide content on mortar as a function of time, it can be observed (see Fig. 2) that the quantity of CH decreases significantly for a Portland pozzolan cement containing 20% of pozzolanic material, compared to pure Portland cement.

Fig. 2 Calcium Hydroxide Content of Pozzolanic Cement and Portland Cement Mortar



3.5 Standards for mineral components

The increased use of mineral components in cement and concrete brought to the development of specifications describing the characteristics of the different materials and the testing methods applied to evaluate suitability of use in cementitious blends.

These features are usually enclosed in the main cement standards (e.g. ENV 197/1 on common cements, ASTM C-595 on blended cements). When the mineral component can be directly used in the mix design of concrete, specific standards are usually drafted.

A comprehensive description of national and international specifications for blended cements and their mineral constituents is given in the chapter on cement standards.

As an example, some of them are listed below.

- ◆ **ASTM C 311** "Sampling and Testing Fly Ash or Natural Pozzolanas for Use as a Mineral Admixture in Portland-Cement Concrete"
- ◆ **EN 450** "Fly Ash for Concrete"
- ◆ **ASTM C 989** "Specification for Ground Granulated Blast Furnace Slag for Use in Concrete and Mortar"
- ◆ **ASTM C 1240** "Specification for Silica Fume for Use in Hydraulic Cement Concrete and Mortar".

As concerns the question whether it is more advisable to use mineral components in the manufacture of blended cements rather than in the preparation of concrete mixes, the theoretical answer is quite simple. The important thing is that both concretes, the one prepared with a blended cement and the other prepared by addition of the mineral component directly into the concrete mixer, prove to be equivalent in performance. From a practical point of view, facts in favour of the use of a blended cement are a well established quality control on materials, availability of large storage facilities that smoothen quality fluctuations, possibility to adjust the cement composition and production parameters to the desired final binder performance.

3.6 Testing methods

The most currently used testing methods for the determination of the quality of an addition are:

- ◆ Chemical analysis including heavy metals and insoluble residue
- ◆ Mineralogical analysis by means of XRD and microscopy
- ◆ Calorimetric methods such as DTA, DSC or TGA
- ◆ Particle shape (microscopy)
- ◆ Density
- ◆ Fineness and particle size distribution (Blaine, sieve analysis, laser granulometry)
- ◆ Grindability ('Holderbank' grindability test)
- ◆ Activity index and pozzolanic activity determination:
 - Keil Index (hydraulic)
 - Strength Activity Index (SAI) according to ASTM C 311
 - CEN pozzolanic activity test
- ◆ Test on standard laboratory cement
- ◆ Specific accelerated mortar test, etc.

A combination of 2 or 3 of the above methods is generally necessary for the current quality control of acceptance of an addition.

4. MAIN MINERAL COMPONENTS FOR PRODUCTION OF BLENDED CEMENTS

4.1 Blast furnace slag - other slag types

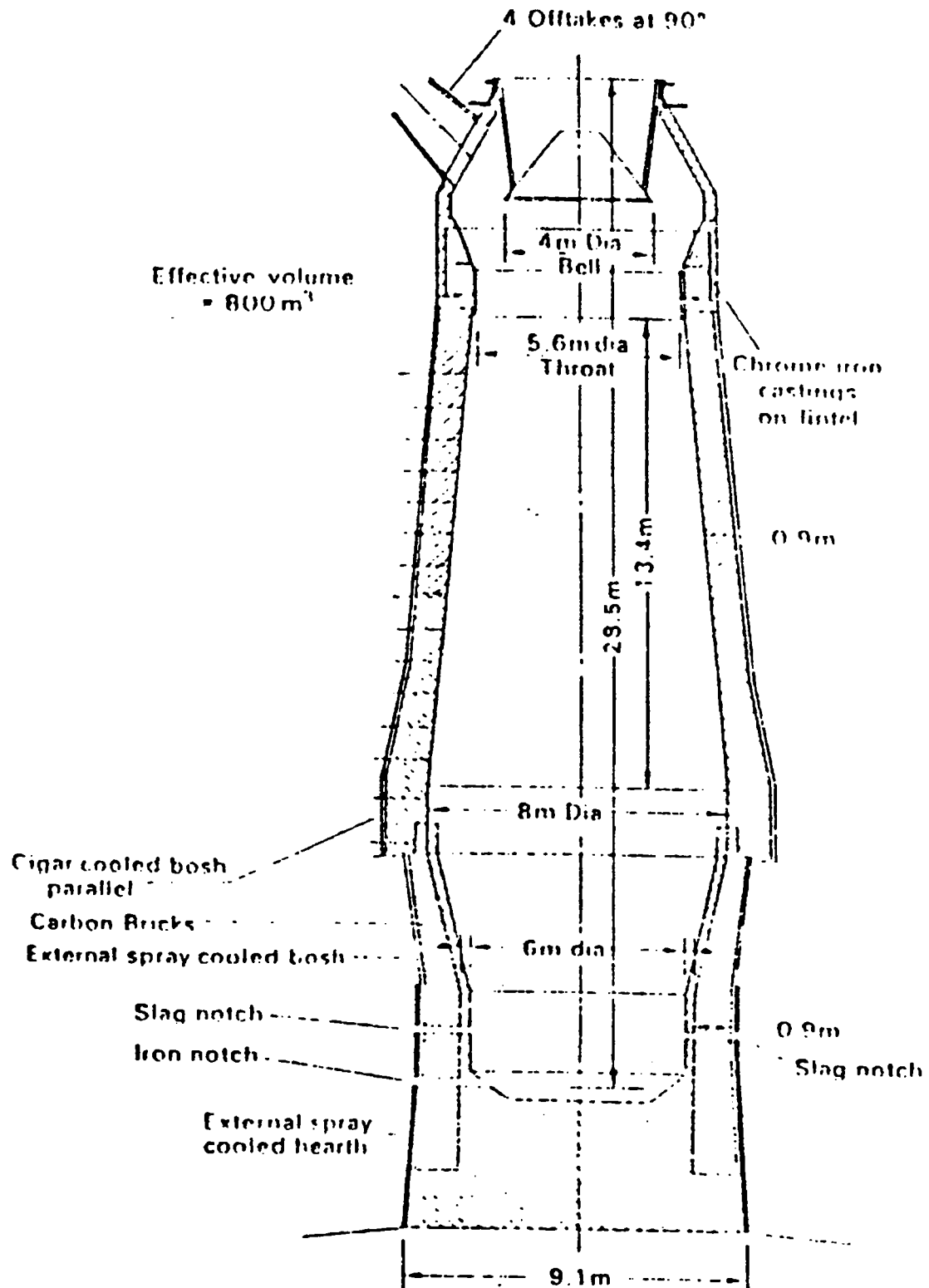
Slags are obtained as by-products in industrial processes of the metallurgic industry.

When metal is extracted from its ore and refined by a further process, slag of various qualities are obtained. The most important slags are those of the iron-melting operations, above all the blast furnace slag. These slags can be considered as the molten silicate complex, formed by a combination of agglomerated earthy matter with the ore, fuel and fluxes either in, or added to the charge. All the slags are molten in the furnace hearth. The chemical and mineralogical composition of the slag varies according to the raw materials and the refining process.

4.1.1 Production of Blast Furnace Slag (BFS)

In the blast furnace, iron ore is converted into pig iron. The slag floats on the top of the liquid iron and is drawn off through a notch (see Fig3).

Fig. 3 Sectional Diagram of a Modern Blast Furnace



Blast furnace slag consist of secondary constituents of the iron ore, the combustion residues of coke and the necessary additions such as limestone or dolomite.

The iron ore is mainly a mixture of oxides of iron, silica and alumina. The chemical reactions within the blast furnace reduce the iron oxide to iron. The silica and alumina compounds react and combine with the calcium added as a fluxing stone (limestone and dolomite) to form the slag. The chemical reactions occur at temperatures between 1300 and 1600°C.

The limestone and dolomite are calcinated at this temperature, and the resulting calcium and magnesium oxides are combined with the silica and alumina of the iron ore to form a slag. Compounds of lime-silica-alumina and magnesia are formed in a similar way as during the clinkering process in a cement kiln.

To ensure a constant quality of iron, the feed of the furnace must be uniform and therefore the composition of the slag varies only slightly as well as in a good conducted melting process. For an economic production of iron, it is essential that the ratio of slag volume to pig iron volume is as low as possible. Modern plants should have an average ratio of 200 to 300 kg slag per ton of iron.

The density and porosity of the slag depends on the conditions of cooling, as well as on its chemical composition. According to the cooling process, different slag types can be distinguished (see Fig.4).

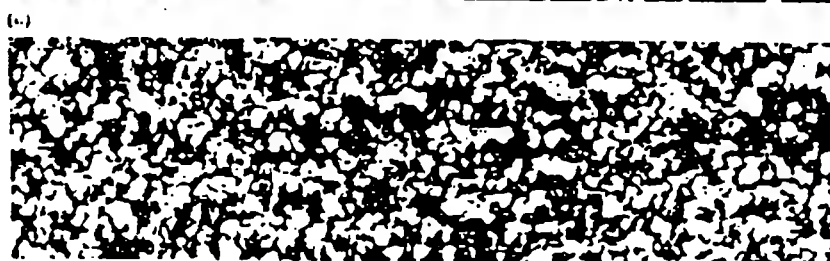
Fig. 4 Forms of Blast Furnace Slag



air cooled



foamed
(or exposed)



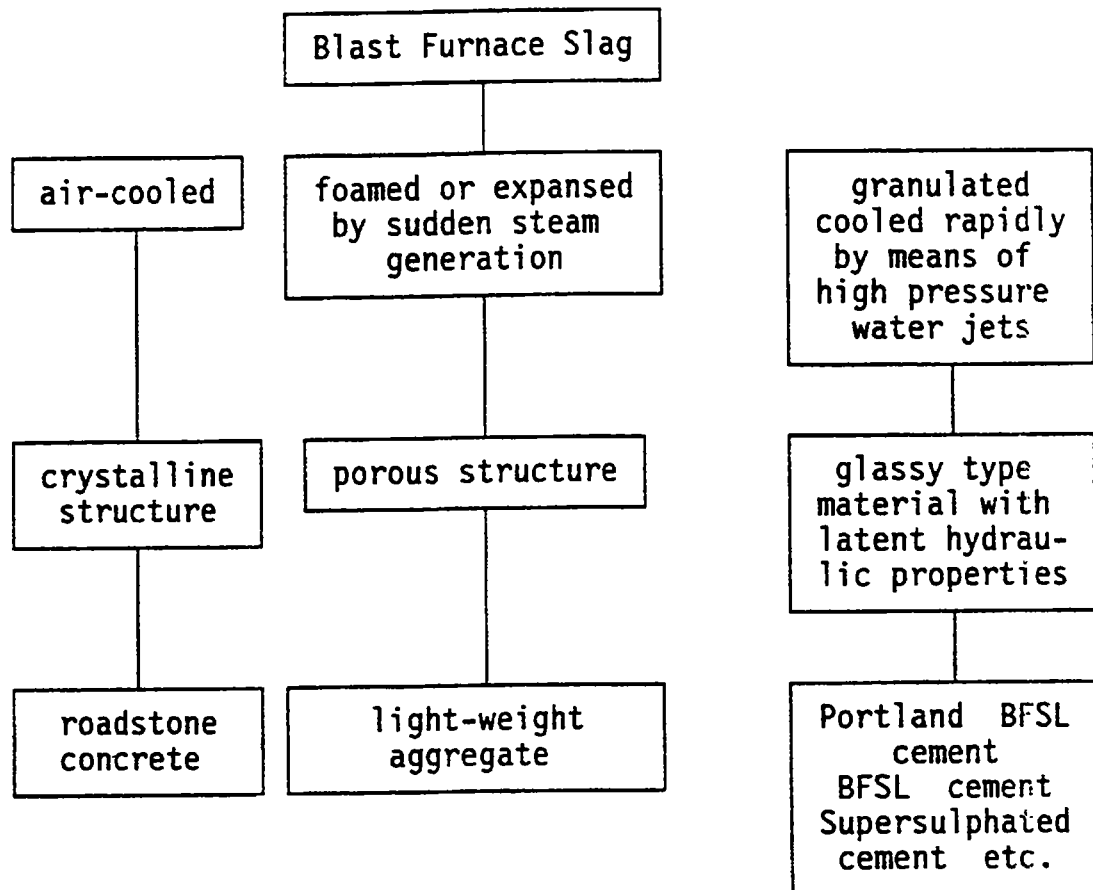
granulated

Air-cooled, crystalline BFS is hydraulically not active and therefore is used as an aggregate or filler.

The high energy of the slag melt is completely dissipated in the case of slow cooling, and a stable crystalline product is formed with properties similar to those of basalt. It is used in road base constructions or as concrete aggregate. Crystalline slags have very weak or no cementitious properties.

Granulated, rapidly cooled, glassy slag has latent hydraulic properties, i.e. it can be activated so that a cement is obtained.

If the slag is cooled rapidly, a slag glass, richer in energy and with cementitious properties is obtained.



Today, there are basically two methods of rapid cooling of slag:

- ◆ Granulation
- ◆ Pelletization

4.1.1.1 Granulation Method

By the traditional well-established granulation method, the slag is first divided into small droplets, up to 5 mm in size, which subsequently are brought into contact with air or water. The use of compressed air has the advantage for the cement industry that a dry product is obtained, however, a lower glass content in slag results. Therefore, granulation is mostly done with water, whereby a quantity of up to 10 m³/t of slag is required. By applying spray jets, only about 3 m³ water per ton of slag are necessary. It is important that the cooling rate is high (down to 800°C) in order to maintain the glassy state of the slag. In the granulation process, the water content may be undesirably high (up to 30%), the excess water is then partially removed during storage in gravel filter basins. The final moisture content is usually still too high (≥ 10%) for direct grinding with clinker at proportions above 20%, thus a slag drier has to be installed.

4.1.1.2 Pelletization Method

The pelletization method was advanced in Canada. In this procedure the molten slag is pre-cooled with water and hurdled into the air by a rotary drum to separate it into two different fractions. The larger pellets (up to 15 mm) which have a lower glass content are used as light-weight aggregate.

The smaller fraction (up to 5 mm) with a higher glass content is reported to be suitable for the production of blended cements. The advantages of this process are the lower water consumption and the lower residual water content of the slag (less than 10%). The hydraulic activity and the grindability do not differ from that of granulated slag.

4.1.2 Properties of Slag

It is generally agreed that in the manufacture of slag for cementitious purposes high CaO content is beneficial to the development of strengths. However, the CaO/SiO₂ ratio can only be increased to a limited degree, since under constant operating conditions, increased CaO content results in an increased slag viscosity necessitating higher operating temperature, which in turn affects costs.

At constant basicity, the higher alumina content has a favorable effect on the strength development of activated granulated slag. Iron and manganese oxide and sulfides generally have an adverse effect on strength development.

Magnesium is not present in form of periclase, in either of the slag types, and therefore does not affect the soundness of the hardened concrete. MgO content up to 20% are permissible in slag.

The increase of silica content reduces grindability, and the presence of metallic iron increases the milling time.

4.1.3 Chemical Characteristics and Properties

Many researchers have attempted to define the hydraulicity of slag in terms of chemical formulae based on the observed effects of the various oxides on the compressive strengths of slag cements.

The usefulness of calculated empirical formulae is questionable and the only fixed line guide is the strength development in cement.
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The main proposed moduli relating to BFS in the manufacture of Portland cement are:

- ◆ I - according to DIN 1164

$$\frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2} \geq 1$$

- ◆ II - EN Standard

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2} \geq 1$$

- ◆ III - Keil

$$\frac{\text{CaO} + \text{CaS} + \frac{1}{2} \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2 + \text{MnO}} \geq 1.5$$

$1.5 \leq F \leq 2.0$ good hydraulic properties

$1.0 \leq F \leq 1.5$ poor hydraulic properties

- ◆ IV - Langavant Index

$$i = 20 + \text{CaO} + \text{Al}_2\text{O}_3 + \frac{1}{2}\text{MgO} - \text{SiO}_2$$

$i \leq 12$ poor hydraulic properties

$12 \leq i \leq 20$ acceptable hydraulic properties

$i \geq 20$ excellent hydraulic properties

(slag difficult to granulate)

- ◆ V - Basicity Index

$$1.20 \leq \text{CaO} / \text{SiO}_2 \leq 1.5$$

- ◆ VI - Silica-alumina Ratio

$$1.8 \leq \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3} \leq 1.9$$

Lea has commented on the usefulness of such empirical formulae: 'Chemical composition moduli are convenient for the rapid control of slag quality, but the only fixed guide is the strength development in cement'.

4.1.4 Mineralogical Composition

The chemical composition of slag is not significant enough to predict their behaviour.

Much more important than chemistry, is the mineralogy of slag, and principally the proportion between the crystalline and the glassy phase. A good slag shall contain at least 2/3 by mass of glassy slag, according to EN standard.

The following methods are applied to determine the mineralogical properties:

- ◆ Microscopy
- ◆ X-ray diffraction (XRD)
- ◆ Differential thermal analysis

By differential thermal analysis, vitreous slag shows irreversible exothermic peaks at about 860°C, when heated between 800 and 900°C. These peaks are mainly due to the heat of devitrification of the glassy part of the slag. Some authors tried to find a correlation between the areas under the peaks and the slag content.

By X-ray diffraction, crystalline materials produce strongly marked peaks. The following Fig.5 gives the pattern of a crystalline and an amorphous slag.

The most commonly occurring minerals found in blast furnace slag are given in Table 5.

Table 5 Commonly occurring Minerals in Blast Furnace Slag

Mineral	Formula	Analysis (% by mass)			
		SiO ₂	Al ₂ O ₃	CaO	MgO
Gehlenite*	2CaO . Al ₂ O ₃ . SiO ₂	21.9	37.2	40.9	14.8
Akermanite*	2CaO . MgO . 2SiO ₂	44.1		41.1	
Wollastonite	CaO . SiO ₂	51.7		48.3	
C ₂ S	2CaO . SiO ₂	34.9		65.1	
Rankinite	3CaO . 2SiO ₂	41.7		38.3	
Merwinite	3CaO . MgO . 2SiO ₂				25.8
Anorthite	CaO . Al ₂ O ₃ . 2SiO ₂	43.2	36.6	20.2	
Monticellite	CaO . MgO . SiO ₂	38.4		35.8	
Spinel	MgO . Al ₂ O ₃				

* These compounds form a continuous series of solid solutions known as melilite

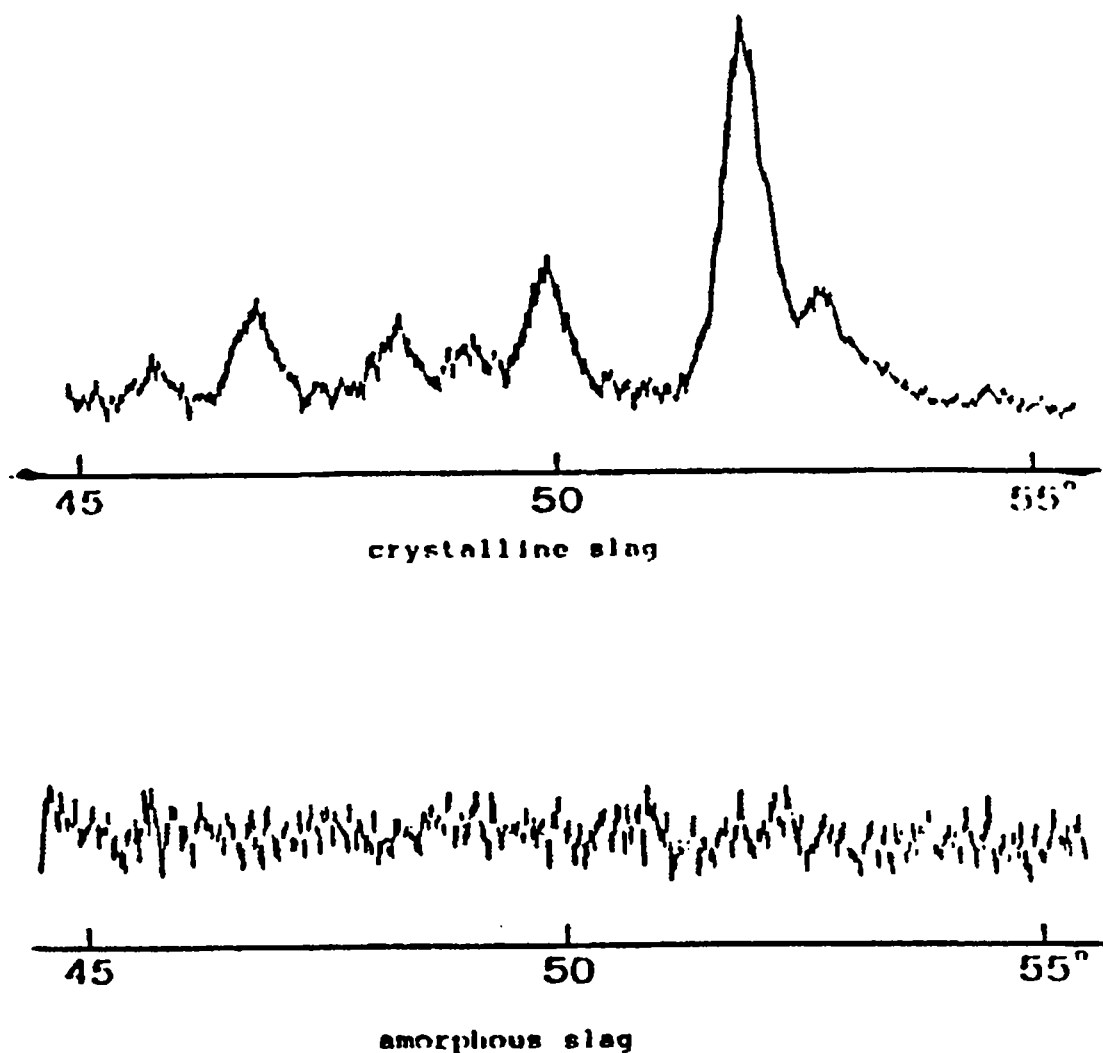
The most common mineral is melilite, a name applied to any of a series of solid solutions from akermanite, which is represented by 2CaO . MgO . 2SiO₂, to gehlenite 2CaO . Al₂O₃ . SiO₂. In slag of low lime and high alumina content, the mineral anorthite CaO . Al₂O₃ . 2SiO₂ may appear.

In slag with a high lime content, the CS may be formed: This compound occurs in three different forms: α, β, γ. The α-form occurs at temperatures above 1420°C.

When the temperature drops to about 675°C, the CS occurs in the β-form. At atmospheric temperature, the β changes into the γ-form, increasing a volume of about 10%. If the silicate is present in sufficient quantities, this expansion causes disintegration of the slag matrix. To avoid this, the lime has to be limited (generally, limitation of the CaO/SiO ratio to 1.4 in some countries).

The specific gravity of crystalline slag lies between 2.38 and 2.76, the bulk density between 1150 and 1440 kg/m³.

Fig. 5 **XRD of Slag**



4.1.5 Other Types of Slag

Other types of slags than iron blast furnace slag have been introduced in the EN standards and are admitted for the production of Portland blended cements, with a maximum content of 15%.

The chemical composition of slags produced as a by-product in the metallurgical industry varies within a very wide range and depends on their origin. Typical analysis from different metallurgical industries have been compiled by Smolczyk and are given in Table 6.

Table 6 Characteristic Composition of Metallurgical Slags

	Non-ferrous Slags				Ferrous Slags	
	Lead Zinc U.K.	Nickel Canada	Copper S. Africa	Phosphorus Furnace USA	Steel BOF (LD Slag) Germany	Iron Blast Furnace Europe
SiO ₂	18	29	34	41	13	34
CaO	20	4	9	44	47	41
MgO	1	2	4	1	1	7
Al ₂ O ₃	6	1	6	9	1	13
FeO _x + MnO _x	38	53	41	1	31	1
CaO/SiO ₂	1.1	0.1	0.3	1.1	3.6	1.2

4.2 Fly ash - Coal ash

4.2.1 Production of fly ash

Fly ashes are obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases from furnaces fired with pulverized coal.

The pulverized coal is injected into the furnace in a stream of air sufficient for the combustion of coal. The remaining particles after burning of the coal are collected in the electrostatic precipitator in form of a cement like powder as fly ash. Part of the ash is collected at the bottom of the furnace as bottom ash (see Fig. 6).

Fly ashes may be silicoaluminous or silicocalcareous in nature. The former have pozzolanic properties, and the latter have, in addition, hydraulic properties.

Fly ash is a mixture of mineral components which have undergone thermal transformations and which contain still unburnt materials. The main component is an aluminium-iron melt, in which the silica and other oxides are dispersed in a molecular form.

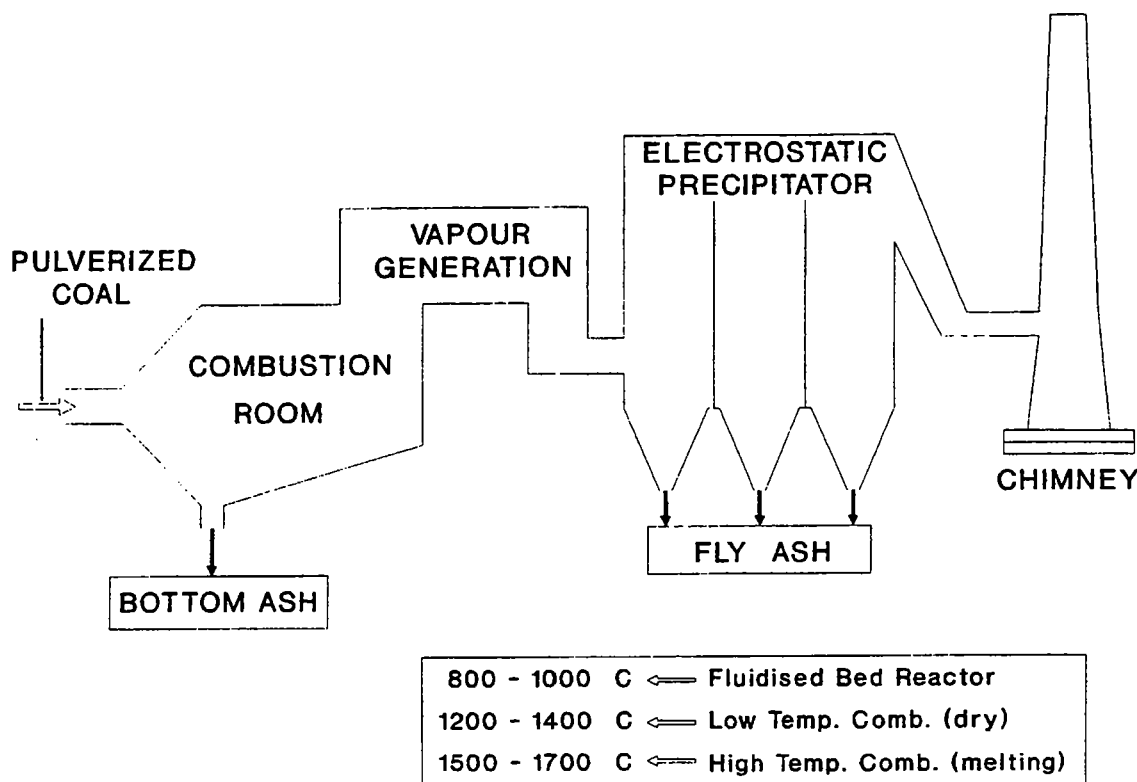
According to the burning temperature of the coal, three types of fly ash may be distinguished:

- ◆ Type I: Burning temperature 800 to 1000°C
 - crystal structure remains
 - about 20% of the fly ash is melted
 - poor pozzolanic properties
- ◆ Type II: Burning temperature 1200 to 1400°C
 - most minerals are melted (about 70%)
 - about 60% of melted particles are deposited before reaching the precipitator, only 40% get to the filter
 - slow reaction with Ca(OH)₂, only medium pozzolanic activity
 - grain size distribution similar to cement
 - can replace 10 to 30% of cement
- ◆ Type III: Burning temperature 1500 to 1700°C
 - all minerals are melted
 - grain size distribution similar to cement
 - rapid cooling of the fly ash induces the production of 60 to 80% of glassy particles

- development of good pozzolanic properties

It is generally known that the volume of fly ash produced in most countries exceeds largely the volume that can be utilized, but statistics are generally unavailable.

Fig. 6 Coal Fired Power Station



4.2.2 Properties of Fly Ash

The ash quality depends greatly on the type of coal, type of process and actual operation of the furnace. The operating conditions as well as the coal quality strongly influence the variability of the ash with respect to residual carbon content, composition and pozzolanic activity.

Fly ash burnt at high temperatures are best suited for the production of blended cements, where the pozzolanic activity is important. Other uses of fly ash, where pozzolanic properties are less important, are:

- ◆ Light-weight aggregate
- ◆ Foamed concrete
- ◆ Macadam, etc.

4.2.3 Chemical and Physical Properties

The main chemical components of ashes are SiO_2 , Al_2O_3 , Fe_2O_3 and CaO . Substantial amounts of alkalis and sulfate may also be present. In the case of lignite or brown coal, the observed amount of free lime as well as of anhydrite is generally high. Significant amounts of periclase can also be noticed in lignitic fly ash. The typical aspect of fly ash observed by microscopy is given in Phototable 1, while Fig. 7 shows the grain size distribution obtained by laser granulometer.

Phototable 1 Thin Walled Hollow Sphere of Fly Ash (Scanning Electron Micrography)

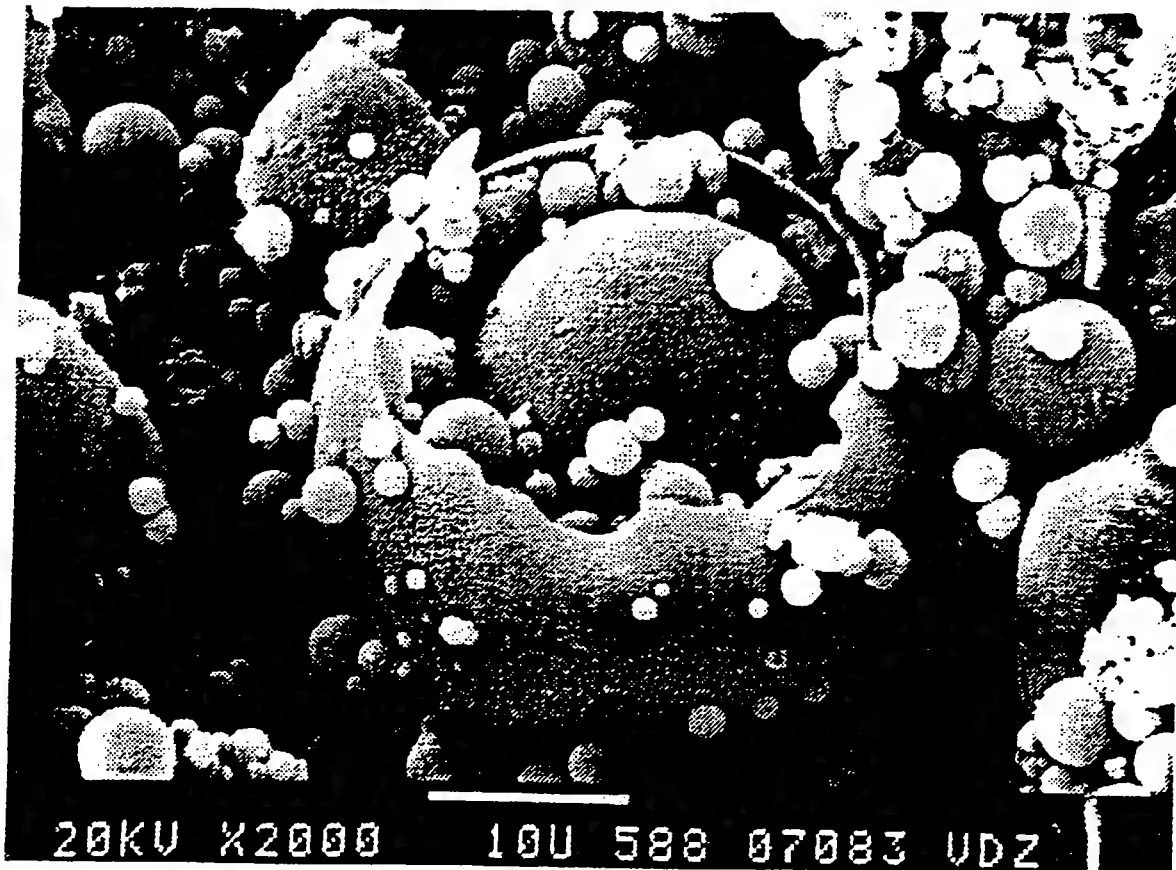
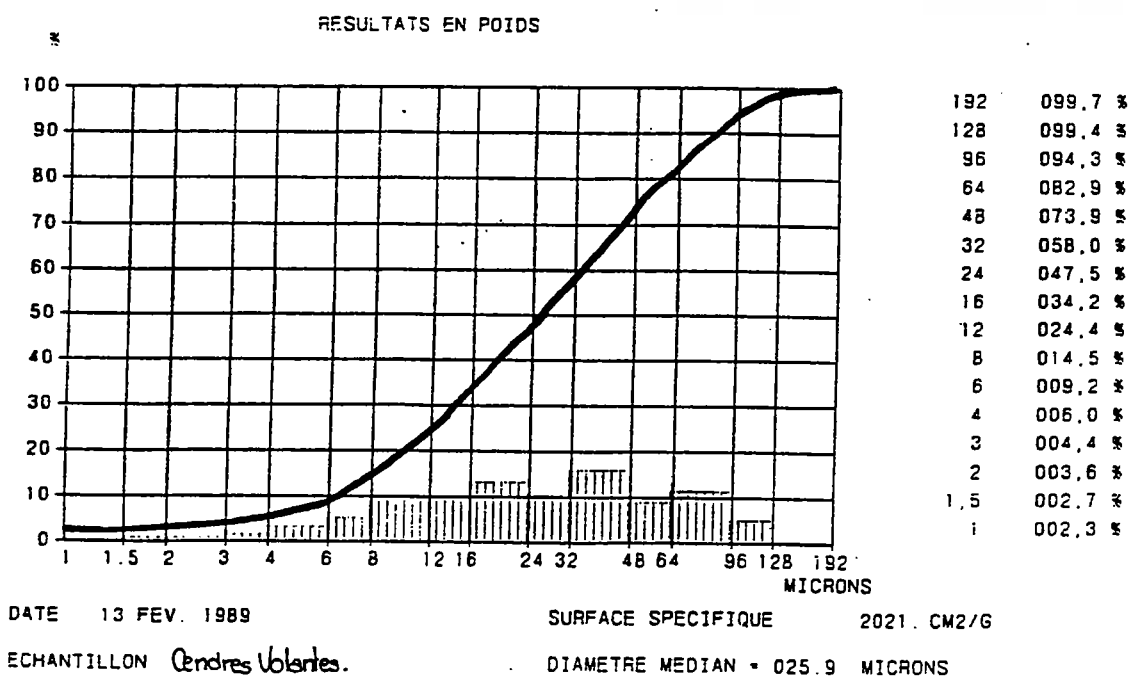


Fig. 7 Granulometry of fly ash



4.2.4 Mineralogical Properties

The mineralogical composition of fly ashes depends on the amount of glassy material. The following minerals can be observed (Table 7), depending on the operating conditions and type of coal. Moreover, calcareous fly ash possess hydraulic properties, due to a more or less greater amount of dicalcium silicate CS.

Table 7 Mineralogical Composition of Fly Ash

Minerals	Quantity % in weight
Glass	70 - 98
Quartz	1 - 15
Mullite	1 - 10
Magnetite	1 - 8
Hematite	1 - 5
Calcite	< 2
Plagioclase	< 2
Merwinite	< 2
Melilite	< 2
Anhydrite	1 - 8
Free lime	1 - 8
Periclase	1 - 6
Wollastonite	1 - 5
Dicalcium silicate	1 - 15

4.2.5 Carbon Content

The carbon content is an important criterion to assess quality of fly ash. Residual carbon is due to the non-burnt organic matter and lies generally in the range of:

- ◆ 1 to 12% in anthracitic fly ash
- ◆ 1 to 4% in lignitic fly ash

The variations in C-content are mainly due to instabilities of the burning system, to variations in burning intensity or to changes in coal supply.

A high carbon content (> 5%) is considered detrimental for the quality of concrete since it might

- impair the air-entrainment in freeze/thaw resistant concrete
- have a negative effect on workability and strength development of concrete

From the manufacturing point of view, it is worthwhile mentioning that most of the unburnt material is agglomerated and concentrated in the coarse fraction of fly ashes. Recent developments in the technology of fly ash beneficiation allow to improve quality by mechanical or electrical separation of the organic matter, making it possible to use high-carbon fly ashes (separated unburnt coal can be used as additional fuel for clinker burning).

4.2.6 Classification

Fly ash can be classified according to EN 197 or to ASTM C 618 in the following classes of Table 8.

Table 8 Classification of Ashes

Characteristics	ASTM	EN
Fly ash from anthracite or bituminous coal Siliceous fly ash	Class F	Class V
Fly ash from lignite or subbituminous coal	Class C	
Calcareous fly ash		Class W

4.2.7 Requirements

The requirements does not significantly differ between ASTM and EN standards. Table 9 summarizes the ASTM chemical requirements, whereas those for EN are given in Table 10.

Table 9 ASTM Chemical Requirements

Specifications	Class F	Class C
- Silicon dioxide (SiO_2) + Aluminium oxide (Al_2O_3) + iron oxide (Fe_2O_3), in % weight	70.0	50.0
- Sulfur trioxide (SO_3), max. %	5.0	5.0
- Moisture content, max. %	3.0	3.0
- Loss on ignition, max. %	12.0	6.0
Supplementary optional chemical requirements (apply only when specifically requested)		
- Magnesium oxide (MgO), max. %	5.0	5.0
- Available alkalis, as NaO_2 equiv., max. %	1.5	1.5

Table 10 ENV 197-1 Requirements

Specifications	Class V	Class W
- Loss on ignition, max. %	5.0	5.0
- Reactive CaO , %	< 5.0	> 5.0
- Reactive SiO_2 and Al_2O_3 , %	> 25	
- Expansion (Le Châtelier)		< 10 mm
- Compressive strength: 30% W FA + 70 OPC		> 10 N/mm^2

4.3 Pozzolanas

4.3.1 Definition

Pozzolanic materials are natural or industrially activated products.

Pozzolanas are siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious properties. When finely ground, they react in the presence of water at ambient temperatures with dissolved calcium hydroxide Ca(OH)_2 from lime or Portland cement clinker to form strength developing calcium silicate and calcium aluminate compounds.

Natural Pozzolanas are mostly of volcanic origin and they can be found in various parts of the earth. The Pozzolanas were named after the Italian town Pozzuoli, near Mt. Vesuvius. Other well-known Pozzolanas are the German 'trass' and the Greek 'Santorin earth'. But Pozzolanas are obviously available in a great number of other countries.

The Romans used Pozzolanas together with burnt lime as building materials, hardening either in air, or even under water. Many remainders from that time prove the good quality of these materials. When Portland cement was invented (in the 19th century), the Pozzolanas fell into oblivion, but today, due to the high cost of fuel, the pozzolan regained their importance.

There are two great families of Pozzolanas:

- ◆ Natural Pozzolanas
- ◆ Artificial Pozzolanas

The natural Pozzolanas are mainly of volcanic or metamorphic origin or of other highly siliceous materials such as diatomaceous earth.

Typical examples of natural Pozzolanas are:

- ◆ Volcanic ashes or pumicites
- ◆ Diatomaceous earth
- ◆ Opaline cherts and shales
- ◆ Tuffs, phonolites, zeolites, etc.

The artificial Pozzolanas are produced by means of thermal treatment from non-pozzolanic material (e.g. marl, shale) or from material with very low pozzolanic properties (e.g. phonolite). When exposed to a rise of temperature, depending on the nature of the raw material (150°C to about 1500°C), they are activated (crystalline structure is modified and glass is formed) and therefore develop pozzolanic properties.

Clay-bearing Pozzolanas, altered volcanic ashes and tuffs as well as shales need a calcination at temperatures between 500 and 1000°C, in order to be activated.

4.3.2 Classification of Natural Pozzolanas

A tentative classification of the natural Pozzolanas according to the nature of the reactive constituents is difficult. They can, however, be distinguished in four great groups. An aspect of natural pozzolan by SEM is given by Phototable 2.

4.3.2.1 Glassy Volcanic Rocks

Those rocks consist of loose or consolidated rocks of volcanic origin, the predominant component being unaltered glass. The reactive glass originates from explosive eruptions where abrupt cooling took place preventing crystallization (e.g. pumice). The vitreous particles have a very high internal surface promoting reactivity. The presence of alkalis favors a more open glass structure and thus, a more reactive type of pozzolan. Volcanic ashes also belong to this group, the minute particles having been quenched in the atmosphere.

4.3.2.2 Zeolitic Volcanic Rocks

Zeolitic volcanic rocks consist of loose or consolidated materials of volcanic origin. The reactivity is mainly due to the inclusions of zeolites or to the partially zeolized glass which is very sensitive to any type of reaction.

This group comprise also the highly siliceous material which has suffered considerable chemical alterations due to circulation of gases and aqueous solutions in the deposit. Natural leaching causes a very high internal surface.

4.3.2.3 Mixed Pozzolanas

Mixed Pozzolanas consist of one of the above mentioned types, mostly mixed with clayey material and other inert minerals.

Gaize and Moler are typical representatives of this group. An increase in their reactivity is mostly obtained by a thermal treatment at low temperature.

4.3.2.4 High Silica Pozzolanas

High silica Pozzolanas are a reactive form of hydrated silica containing mainly skeletons of living organisms such as radiolarites or diatoms. They lead to an extremely porous structure. They are often the host rocks for petroleum and are used as hydraulic additions after extraction of the fuel. A thermal treatment at low temperature is generally recommended for a considerable increase of their reactivity.

4.3.3 Chemical and Mineralogical Composition

Pozzolanas - natural as well as artificial - consist essentially of reactive SiO_2 and Al_2O_3 . The remainder contains Fe_2O_3 and other oxides. They generally contain also a significant amount of alkalis.

It is not possible to calculate meaningful modulus on the basis of chemical analysis, because the chemical parameters which determine the pozzolanic activity vary in a wide range.

The current control of the quality of a pozzolan can be achieved by applying a combination of three different methods:

- ◆ Chemical composition
- ◆ Mineralogical composition
- ◆ Physical properties

A strict classification is difficult and the Streckeisen-diagram (see Fig.) is the most appropriate document allowing a classification and nomenclature of the different natural Pozzolanas. Table shows the great variety of minerals found in the different types of Pozzolanas tested by 'Holderbank' and used in the different plants of the Group.

Pozzolanic activity of natural pozzolan of volcanic origin depends mostly on their:

- ◆ Glass content
- ◆ Content of zeolitic minerals.

The best results were obtained with Pozzolanas containing:

- ◆ Silica rich glass
- ◆ Zeolites such as chabazite, heulandite, natrolite, stibite and wairakite

4.3.4 Standard Specifications

It is obvious that no basis exists for taking the content of any single constituent, or a quantitatively defined physical or chemical characteristic of such a constituent, as a criterion for judging the pozzolanic reactivity of a material.

The main specifications are summarized in the following Table 11 for ASTM. The determination of pozzolanicity of a pozzolanic material is carried out by applying the ASTM C 311 and in Europe the EN 196-5.

Table 11 ASTM Chemical Requirements

Specifications	Class N
- Silicon dioxide (SiO_2) + Aluminium oxide (Al_2O_3) + iron oxide (Fe_2O_3), min % in weight	70.0
- Sulfur trioxide (SO_3), max. %	4.0
- Moisture content, max. %	3.0
- Loss on ignition, max. %	10.0
Supplementary optional chemical requirements. These optional requirements apply only when specifically requested.	
- Magnesium oxide (MgO), max. %	5.0
- Available alkalis, as NaO_2 equiv., max. %	1.5

Several tests have been proposed to determine the activity of pozzolan. These tests are based on an extraction with a mineral acid or an activation with lime or Portland cement. None of them can be considered as a prediction of the compressive strength of concrete containing pozzolanic material.

The conclusion is that the pozzolanic activity is measurable only by strength development of a blended cement or of a concrete mix in the provided proportions.

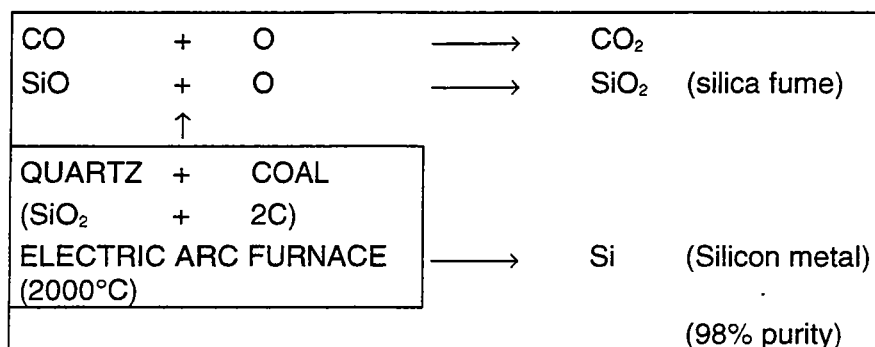
4.4 Silica fume - Other specific pozzolanic materials

As previously indicated, a great number of other industrial by-products or activated materials can be used for the production of blended cements. This paragraph shortly reviews some of them.

4.4.1 Production and Characteristics

Silica fume is a by-product of the manufacture of silicon (see Fig. 9). Silicon is used for the production of ferrosilicon, which is required by the steel industry for the improvement of its products.

Fig. 9 Production of Silica Fume



Condensed silica fume consists of very fine spherical particles with a high content of amorphous silica. It is an extremely fine powder, very much finer than Portland cement or fly ash, its fineness being roughly comparable with the finest particles in tobacco smoke (Table 12).

Table 12 Fineness of Different Materials

Type of Material	Fineness (cm ² /g)
Silica fume	approx. 200'000
Tobacco smoke	approx. 100'000
Fly ash	2'000 to 5'000
Normal Portland cement	approx. 3'000

The grain size distribution is shown in Fig. 10. The extreme fineness gives rise to a number of problems in handling and transporting this material. Its bulk weight is not higher than 300 kg/m³. Exposed piles are stirred by the least breath of wind. Silica fume is either packed in bags as such, or densified and packed in bags, as well as in the form of a 50% water slurry. Transport and transshipment facilities clearly necessitate efficient dedusting systems.

The chemical composition (see Table 13) may vary somehow depending on the impurities of quartz, the features of the manufacturing process, the dust precipitation facilities and the coal used. The effect of different compositions can become quite significant depending on the particular type of application.

Table 13 Chemical Composition of Silica Fume

Elements	Range	
	Min.	Max.
Loss on Ignition	0.7	2.5
SiO ₂	90.0	96.0
Al ₂ O ₃	0.3	3.0
Fe ₂ O ₃	0.2	0.8
CaO	0.1	0.5
MgO	0.5	1.5
NaO	0.2	0.7
HO	0.4	1.0
C	0.5	1.5
S	0.1	0.4

4.4.2 Properties and Requirements

4.4.2.1 *Hydraulic Properties*

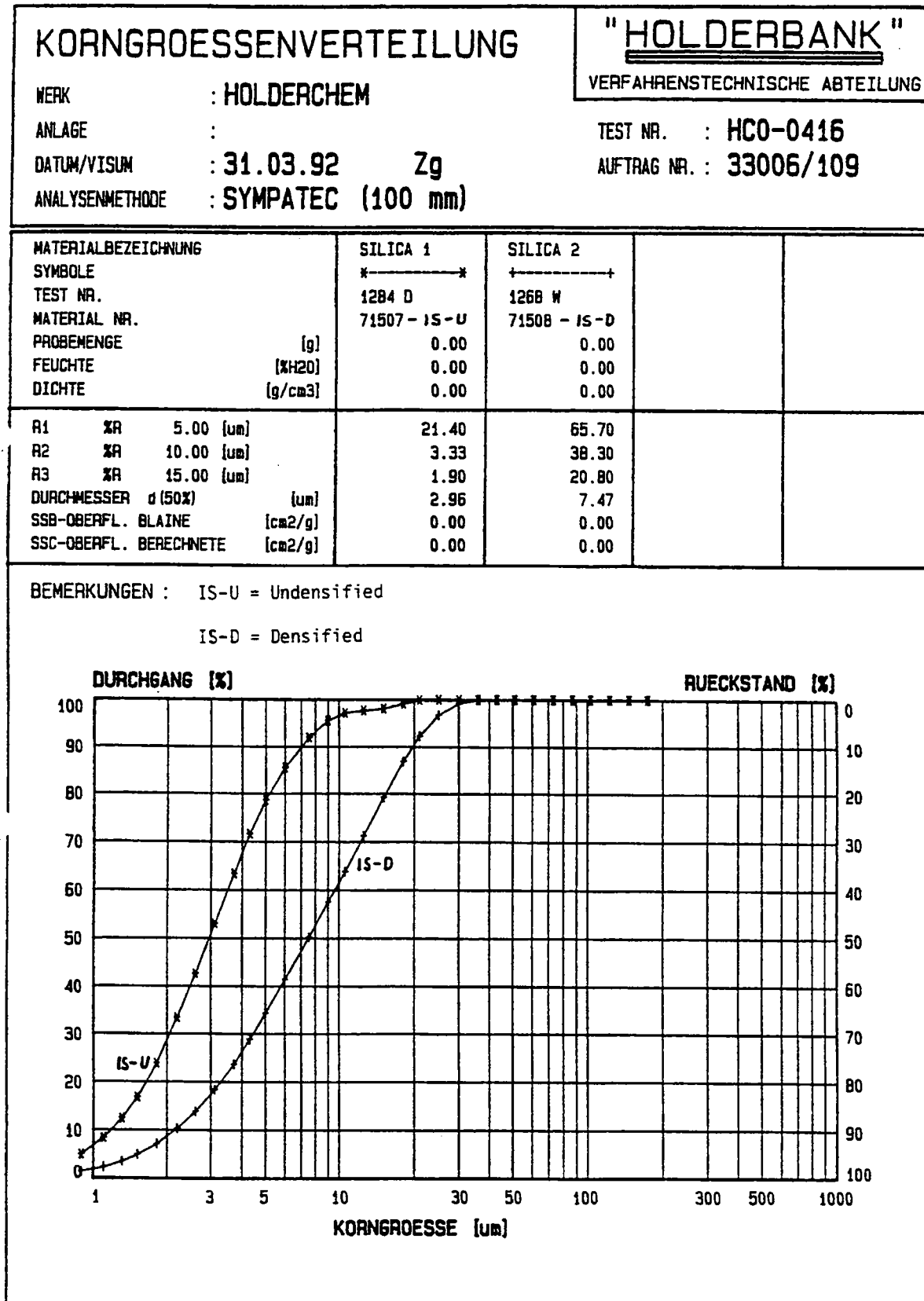
Owing to the great fineness, its completely amorphous state and its high content of SiO₂, silica fume exhibits properties closely resembling those of pozzolan. However, the usual methods for characterizing the pozzolanic activity are not suitable and they had to be first adapted to suit its unusual properties.

4.4.2.2 *Requirements*

Only silica fume that meets the following requirements shall be used:

- amorphous silica SiO₂ \geq 85% by mass
- loss on ignition \leq 4% by mass
- specific surface (untreated) \geq 15 m²/g (BET)

Fig. 10 Grain Size Distribution



4.4.3 Initial Experience

The high pozzolanic activity made it seem obvious to add the silica fume directly to cement or concrete. Tests performed in a great number of laboratories proved that there are a number of problems connected with the handling properties of the silica dust, however, they can be overcome when suitable modifications to the process technology are made.

The level of replacement cement by silica fume is limited and lies generally in the range of $8 \pm 2\%$. The following hardening characteristics (Table 14) have been observed for an ISO standard mortar with a pure Portland cement compared to a 5% silica fume substitution.

Table 14 Characteristics of an ISO Standard Mortar

Strength after ... Days	Pure Portland Cement	95% PC + 5% Silica Fume
2	20.3 N/mm ²	21.4 N/mm ²
28	42.8	54.1
90	53.3	61.2

The amount of water required by the binder is higher and the setting time is generally somewhat shorter compared to pure PC. The increase of strength is remarkable and conduct naturally to the use of silica fume for the production of high performance concrete. In order to reduce the higher water requirement, it is recommended to add superplasticizer in the concrete mix. In spite of its remarkably high price, this material is chosen in most cases where production of a high performance concrete is required.

4.5 Burnt Shale - Calcinated Marls and 'KALSIN'

Burnt shale, in special cases burnt oil shale, calcinated marls and Kalsin (a patented product of the 'Holderbank' Group) are produced in conventional rotary kilns as well as fluidized beds, at a temperature of approximately 800°C. Owing the composition of the natural materials and the manufacturing process, these products contain hydraulic mineralogical phases identical to those produced during the clinkering operation. Those phases are mainly dicalcium silicate and monoaluminate as well as reactive gehlenite and calco-spurrite. Due to the specific burning process (generally under reducing atmosphere) only small amounts of free lime is produced whereas calcium sulfate proportion depends essentially on the sulfur present in the raw material. Beside those hydraulic minerals, large proportions of pozzolanically reacting oxides, especially silica and alumina are present.

In a very finely ground state, burnt shale, calcinated marls and Kalsin show like Portland cement, pronounced hydraulic and in addition pozzolanic properties.

Those products must develop, when burnt only - when tested in accordance with EN 196-1 - a compressive strength of at least 25.0 N/mm² after 28 days. If not they are classified in the category of artificial pozzolan.

The expansion shall be less than 10 mm (Le Châtelier test) in accordance with EN 196-3 in using a mixture of 30% by mass burnt material plus 70% by mass reference cement.

4.6 Burnt clays

After calcination at a relatively low temperature (usually < 800 °C), some clays can be converted to pozzolanic materials, after production of reactive phases by alteration of the original crystalline structure of the clay. The required heat treatment is generally variable, since it depends on the nature and fineness of clays. Both the calcination temperature and time have to be adjusted to get best enhancement of pozzolanic activity.

5. ASPECTS OF MANUFACTURE OF BLENDED CEMENTS

5.1 Grinding of blended cements

For optimum production of blended cements, some important aspects related to the grinding process must be carefully evaluated

- ◆ pretreatment of additions
 - drying
 - preblending
- ◆ properties of the addition
 - grindability
 - strength activity
- ◆ type of grinding
 - compound
 - separate
- ◆ dosing of components.

5.1.1 Pretreatment of additions

The additive may have a considerable moisture content, and drying has to be done prior to or during the grinding process. The dosing facilities should be adequate to allow precise and trouble free operation even in case of very moist and sticky materials.

Depending on the nature and the number of the additions used, preblending of the materials would be necessary to achieve sufficient homogeneity of the component and of the cement itself.

5.1.2 Properties of the addition and type of grinding

5.1.2.1 *Grindability*

The grindability of the components is generally different, even in materials of the same type. Big differences might therefore be justified between different plants, and generally a specific solution has to be found for each plant.

Table 15 summarizes some data, taken out of the annual report, giving information on physical properties and the grinding energy needed for the production of blended cements containing slag, pozzolan or fly ash compared to Portland cement.

Table 15 Average Physical Properties and Grinding Energy for Blended Cements

Material	Density [g/cm ³]	Blaine [cm ² /g]	Grinding Energy [kWh/t]
Clinker	3.18	3135	32.43
Slag	2.90	2980	34.17
Nat. Pozzolan	2.55	6150	20.92
Fly ash	2.45	4405	11.92

This table shows that slag is usually harder to grind than Portland cement clinker, while pozzolanic materials are mostly softer. The advantage of fly ash is that it can be added directly to the separator feed, since most of it is already of the required cement fineness.

This also implies that during grinding of a slag cement, clinker will be ground finer, thus contributing to early strength development, while the slag remains coarser and will react later. Thanks to its glassy nature, slag does not affect water demand and workability and can be used at very high addition rates.

In the case of pozzolanic cements, the very soft pozzolana will concentrate in the fine fraction of cement, thus affecting water demand, workability and early strength development. Proper selection of the grinding equipment (central discharge mills, vertical roller mills) will prevent overgrinding of Pozzolanas and improve cement properties.

When designing a new grinding plant for blended cement manufacturing, the process can be optimized to the requirements. Unfortunately, in most plants blended cements have to be produced in old grinding equipment designed for Portland cement production.

High fineness of silica fume and/or important variability of the fineness of fly ash may be responsible for severe problems of handling, transporting and proportioning. This type of material is generally introduced after the mill, in the output bucket or directly in the separator, in order to provide a good mixing, avoid quality fluctuations and improve mill operation.

5.1.2.2 Strength activity

A mineral component is clearly expected to contribute to strength development of cement. Its strength activity will reflect on cement design and on the proportioning system. Typical dosage of a mineral component ranges between 25 and 40%.

5.1.3 Type of grinding

As already mentioned, grindability of the various components can influence the choice of the grinding system, especially in new plants.

Intergrinding of cement is easier from the point of view of plant design and operation, but requires accurate dosing and might be considerably disturbed by quality fluctuations of the different constituents, also in terms of grindability.

The advantage of separate grinding is that each component can be ground at the optimum fineness, thus enhancing its peculiarities and reducing drawbacks usually associated with improper grinding.

5.1.4 Use of chemical admixtures

Some of the drawbacks of blended cements can be compensated by the use of selected chemical admixtures.

Besides the simple addition of grinding aids especially in the case of high replacement rates with hard to grind materials, more sophisticated quality improvers can be applied

- water reducers/plasticizers
- early strength improvers
- multipurpose admixtures.

5.2 Proportioning

The most important quality requirement of blended cements are usually related to their performance in the different applications.

Some of these properties can be summarized as follows:

- ◆ Satisfactory rheological properties for good workability in concrete and mortar
- ◆ Acceptable setting behavior
- ◆ Adequate strength development and sufficiently high 28-day strength
- ◆ Satisfactory expectations for durability of the resulting concrete, as regards
 - residual porosity and permeability
 - resistance to carbonation
 - freeze-thaw resistance
 - resistance to chemical attack (sulfates, pure water, sea water, weak acids)
- ◆ Acceptance of resulting concrete color
- ◆ Reduction of Alkali Aggregate Reaction (AAR) risks
- ◆ Lower heat of hydration

and all specific properties providing better service or higher performances compared to ordinary Portland cement.

The design of composite cements requires first of all the establishment of clear objectives with respect to product characteristics and performances. Both characteristics and performances must comply to cement standard specifications and test methods as well as for concrete production.

The optimum proportion of mineral additions in blended cements is then to be found as a consequence of the available materials and the related cement standards.

In general terms, slags are usually characterised by a good hydraulic potential and a low water requirement in cement, derived from their glassy nature; these features allow for the production of slag cements with high contents of BFS (up to 95%!).

On the other hand, the amount of pozzolana is a compromise between the minimum amount necessary to combine the hydration lime and produce additional silicate hydrates and the maximum acceptable content due to the softness and high porosity of pozzolanas that yield particles with high water demand, thus affecting cement workability. In this case, a normal range for natural pozzolanas or activated clays in cement is 20-45%.

As a rule of thumb, one shall consider that pure replacement of OPC with a mineral component will cause a loss in early strength of 1.5 times the amount of the addition. That is to say that 20% replacement will drop early strength by approximately 30%. This strength loss can be compensated to a great extent by finer grinding, either the cement as such in case of intergrinding, or the clinker fraction in case of separate grinding and following blending.

Increase of grinding fineness will anyway reflect in higher energy consumption of the mill and could impair some of the cement characteristics, especially water demand. In this respect, the technology of chemical admixtures is capable to provide a selection of suitable products for the various needs. Through the proper use of additions, one can improve mill performance, increase early strength, reduce water demand, improve workability.

6. PROPERTIES AND APPLICATION OF BLENDED CEMENTS

Composite cements permit both replacement of normal pure Portland cement and production of special cements whose manufacture usually entails high production costs. In concrete constructions, composite cements can completely replace pure PC with only few exceptions. In fact, there are countries where no pure PC is produced and all the needs of the construction industry are met by composite cements.

According to the experience of many countries, typically 25 to 40% of clinker may be replaced by fly ash or pozzolan, even much higher proportions of blast furnace slag and around 5% limestone filler or kiln dust, without significantly affecting the characteristics of the cement produced, if compared to an ordinary Portland cement. The production of composite cements provide a good solution for a partial or global elimination of the problem kiln-dust. Such a production requires, however, that additions of reasonable quality are used and that the blending/grinding process is optimally adjusted.

6.1 Reactivity of Composite Cements

The main disadvantage of composite cements is mostly their reduced reactivity, i.e. their slower setting and lower early strength compared to pure PC. For this reason, the fast-setting high grade Portland cement (corresponding to ASTM type III) cannot be replaced completely by composite cements, for example in prefabrication. Special care has to be taken when using composite cements for thin concrete elements, the slow reactivity of the composite cement requires special attention in curing to avoid premature drying out, which would prevent a sufficient degree of hydration, particularly near the surface.

6.2 Influence on Setting Time and Water Requirement

Fig. 11 shows the influence of slag, fly ash and natural Pozzolanas on initial set for laboratory cements, on paste of constant consistency. Slag (SL) give generally a longer initial setting time, whereas addition of pozzolan contribute to a small diminution of initial set. The case of fly ash is more problematic and most of this additive cause a significant and detrimental lengthening of setting time. However, this particularity can be beneficial for the production of road cements where a long initial set is desired.

Fig. 11 Influence of Additions on Initial Set (Laboratory Cements)

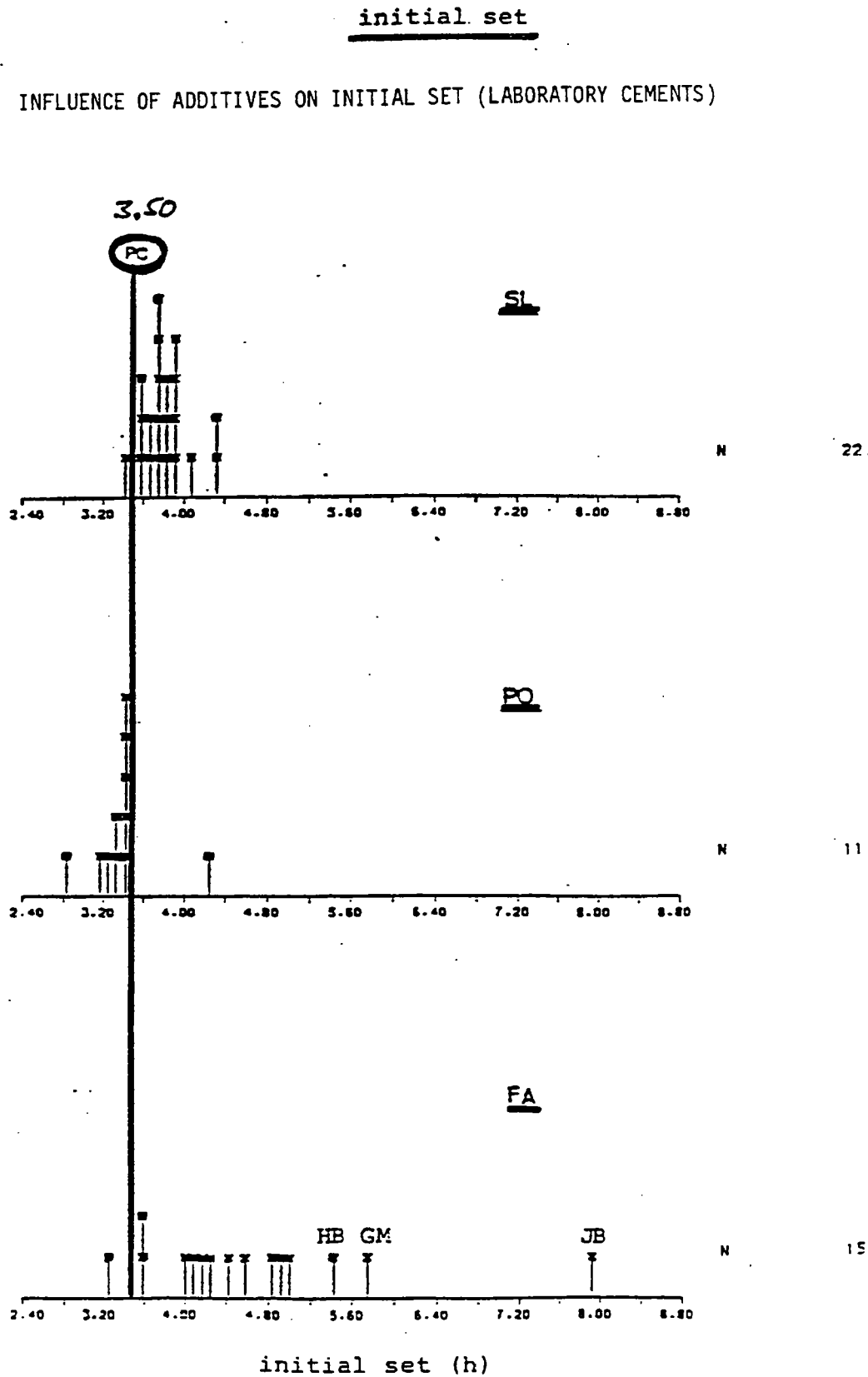
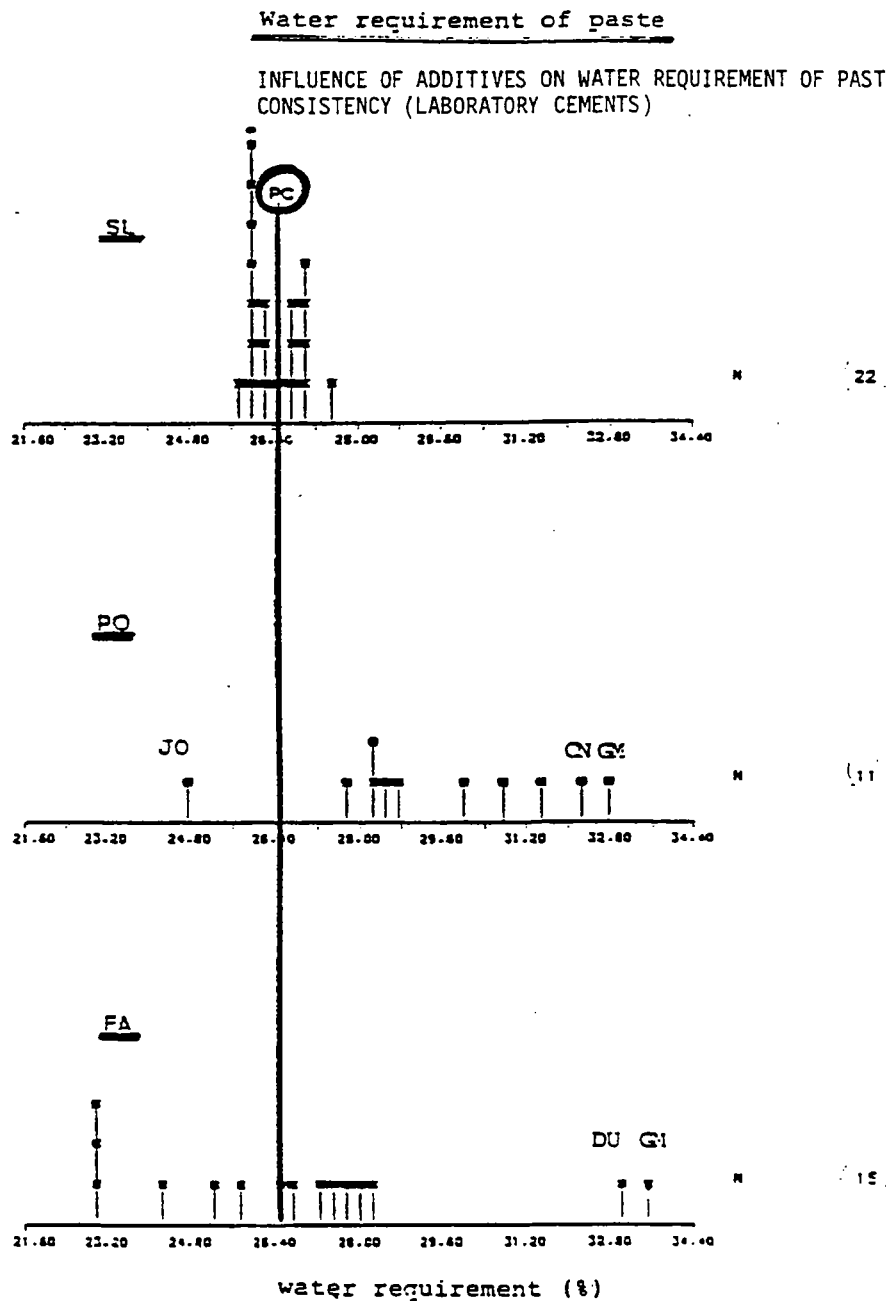


Fig. 12 shows the influence of slag, fly ash and natural Pozzolanas on water requirement for laboratory cements, on paste of constant consistency. If slag has no influence on this parameter, Pozzolanas give generally an important increase of water requirement depending of the nature and grindability of the pozzolanic material. Siliceous fly ash gives generally a decrease of water requirement, whereas calcareous (or lignitic) fly ash show an increase of this parameter which increases proportionally to the calcium content of the ash. The increase of the quantity of spherical particles conduct in most cases to a decrease of water requirement compared to pure PC.

Fig. 12 Influence of Additions on Water Requirement of Paste of Standard Consistency (Laboratory Cements)

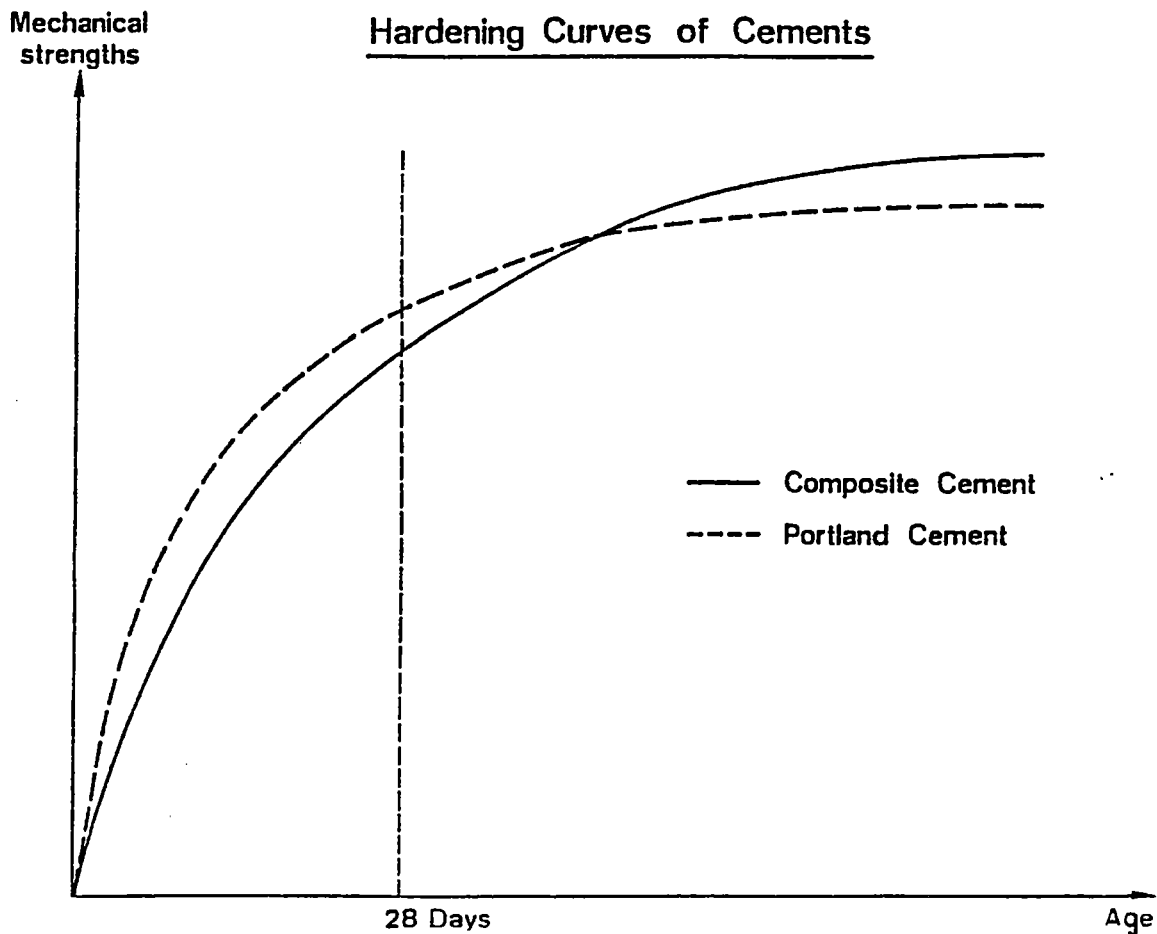


6.3 Other Important Properties

It is well accepted that composite cements are especially suited for mass concrete due to their lower heat development and hardening.

The disadvantage of initial slower strength development, later generally turns out to be an advantage - when correctly cured - for the durability of concrete construction because composite cements usually have a higher strength reserve than pure PC (see Fig. 13), due to the formation of a denser cement matrix which at least offsets the risk of enhanced carbonation due to the lower pH of the matrix.

Fig. 13 Hardening Curves of Cements



Last but not least, composite cements are also recommended for specific applications such as high sulfate resistance, sea water resistance, prevention of alkali-aggregate reaction. In brief, blended cements can be used instead of special, or pure Portland cements where the following concrete characteristics are required:

- ◆ Improved workability (especially fly ash cements)
- ◆ Lower heat development of bulk concrete
- ◆ High to very high final strength
- ◆ Increased water tightness
- ◆ Improved resistance to sulfate and other chemical attacks
- ◆ Lower sensitivity for alkali-aggregate reaction
- ◆ Reduced tendency to unsoundness due to free lime and MgO

Moreover, since slag, fly ash and pozzolan combine with the calcium hydroxide which is formed during the hydration of clinker, the tendency to form efflorescence is diminished.

7. LIMESTONE AND LIMESTONE FILLERIZED CEMENT

Difficulties in the supply of blast furnace slag and fly ash have led cement manufacturers to study the possibility of replacing them by other additions permitted under current standard specifications. Since 1979, French standards have included fillers among those additions that may be used in CPJ cement in a proportion up to 35%.

The recently issued European standard ENV 197/1 allows for the production of two main types of limestone cement, with limestone content of resp. 6 to 20% and 21 to 35%.

The high availability and the low cost of limestone for a cement plant made this type of cement very attractive for most producers, and it is considered opportune to deal with it in a dedicated chapter.

7.1 Properties and advantages of limestone

Limestone filler is an inert material. It produces no chemical effect on the cement in presence of water. It influences the physical properties of cement, and mainly certain features such as:

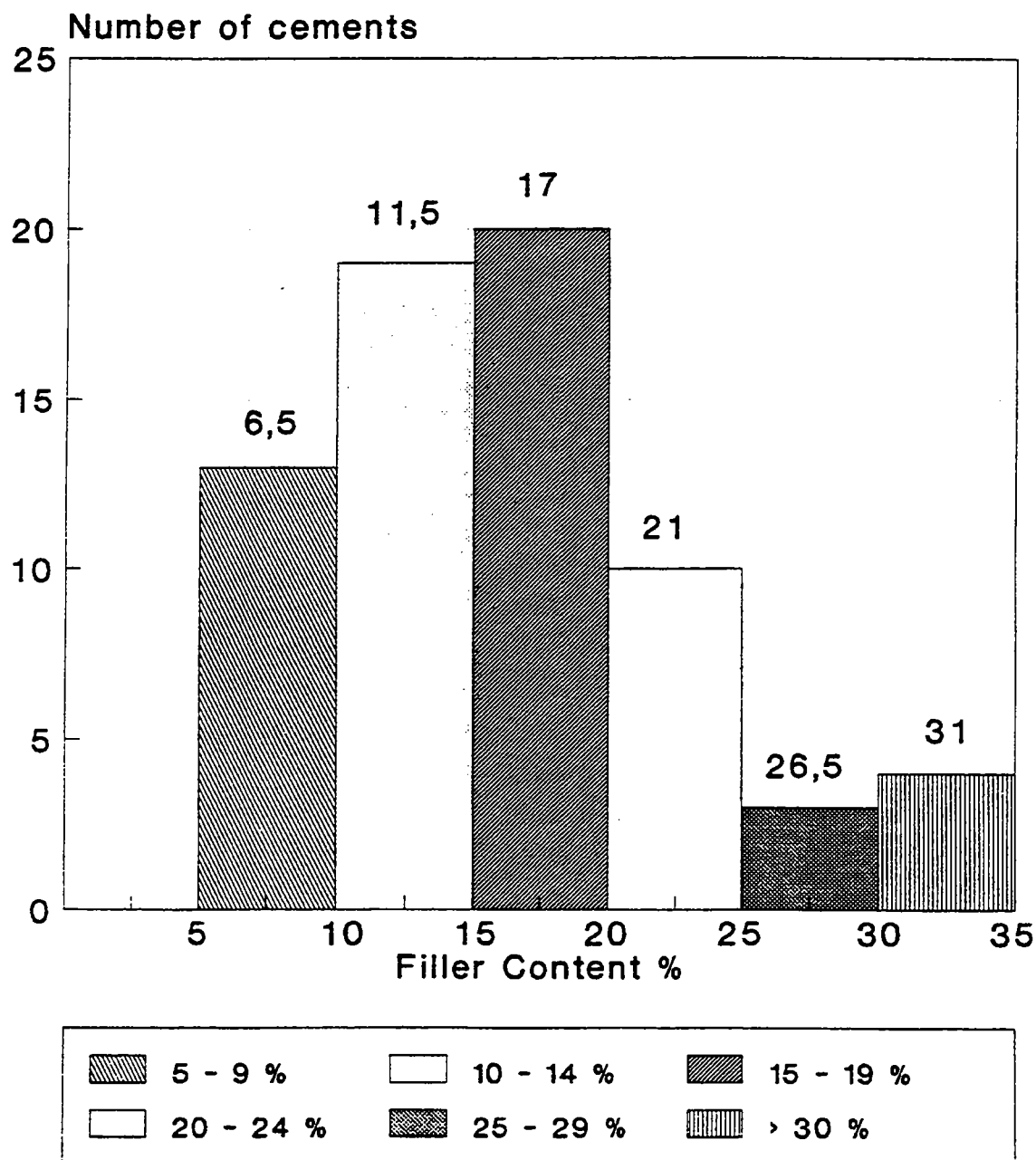
- ◆ Improved workability
- ◆ Reduced permeability and capillarity
- ◆ Higher resistance to cracking
- ◆ Better finishing, etc.

Prior to their introduction on the market, cements containing limestone filler have been subjected to laboratory and industrial trials in order to determine the main characteristics:

- ◆ Mechanical strength
- ◆ Setting behavior
- ◆ Shrinkage
- ◆ Resistance to freeze/thaw
- ◆ Effect on rheology and concrete properties, etc.

Fig. 14 illustrates the distribution of the standardized limestone containing cements in France in October 1992, according to their individual filler content. The data are collected from 68 cements containing between 5 and 32% filler, the mean filler content being 15%.

Fig. 14 Distribution of 68 Limestone Filler Cements: Individual Filler Content



The main reasons for using calcareous additions in the production of blended cements are the following:

- ◆ Cost reduction
- ◆ Scarce availability of mineral components
- ◆ Improvement of cement workability
- ◆ Substitution/complementation of gypsum
- ◆ Differentiation of product
- ◆ Environmental issues

7.2 Standard Specifications - Classification

According to the European standard ENV 197/1, limestone used as a main constituent in cement shall meet the following requirements:

- limestone $\text{CaCO}_3 \geq 75\%$ mass
- clay content methylene blue absorption $\leq 1.2 \text{ g/100 g}$
- organic material content TOC $\leq 0.20\%$ by mass

Clay content has to be limited in order to keep the water requirement of the filler low and avoid a degradation of strength.

The low value of organic material content will eliminate limestone exhibiting cracking risks and micro cracks detrimental to freeze-thaw stability.

Limestone fillerized cements can be subdivided in three main types:

- ◆ Cements (pure Portland or composite) with minor proportions of limestone ($< 5\%$)
- ◆ Portland-limestone cements (5 to 35%, according to EN standards)
- ◆ Masonry cements (up to 75% limestone).

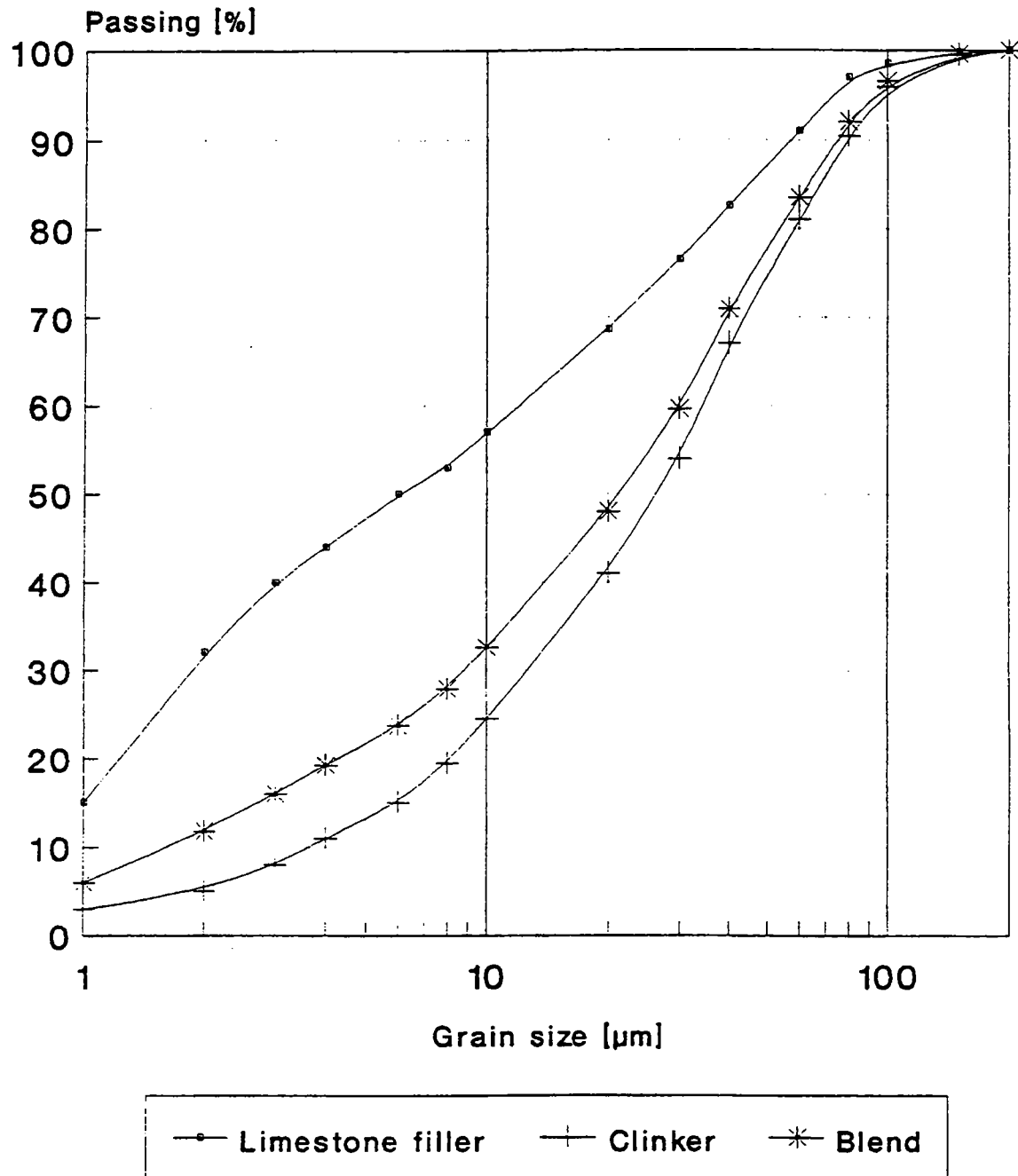
7.3 Cement Properties

7.3.1 Grain Size Distribution

The difference in grain size distribution of the particles when comparing clinker and limestone filler by the intergrinding process is given in Fig.15 for a cement containing 25% limestone. The Blaine fineness of a limestone fillerized cement is greatly affected by the higher quantity of limestone smaller to 10 microns compared to the quantity of clinker. However, the increase of specific surface does not affect (or only very rarely) the required grinding energy.

To explain this, it is worthwhile mentioning that a Blaine measurement is based on a physical property, that is air permeability of a compacted layer of cement at a given porosity. When the composition of cement is changed, by replacing clinker with softer materials, the same particle size distribution of different cements will not necessarily yield the same Blaine fineness, due to the different air flowability characteristics of the cements.

Fig. 15 Grain Size Distribution in Limestone Fillerized Cement



7.3.2 Influence of Limestone on Strength Development

Although limestone filler is an inert material, it was always shown that it has a favorable effect on strength development due to:

- ◆ the better workability
- ◆ the accelerated crystallization of hydrated minerals, more especially aluminates
- ◆ the aggregate bonding properties of the paste.

7.3.3 Consistency and Setting Time

The water requirement for paste and mortar of constant consistency is generally not affected by the incorporation of limestone filler in any major way. Moreover, it was shown that limestone filler can partially replace gypsum without shortening the setting time of the blended cement.

7.3.4 Other Properties

- ◆ The influence of temperature on initial properties remains within the same order of magnitude as that observed with other additions.
- ◆ Shrinkage is similar, or somewhat lower compared to pure Portland cement.
- ◆ The heat of hydration of limestone fillerized cement decreases proportionally with the filler content, the heat of hydration being only affected by the clinker fraction in the blend.

The following Table 16 summarizes the main characteristics of two Portland limestone cements industrially produced in France and in Germany.

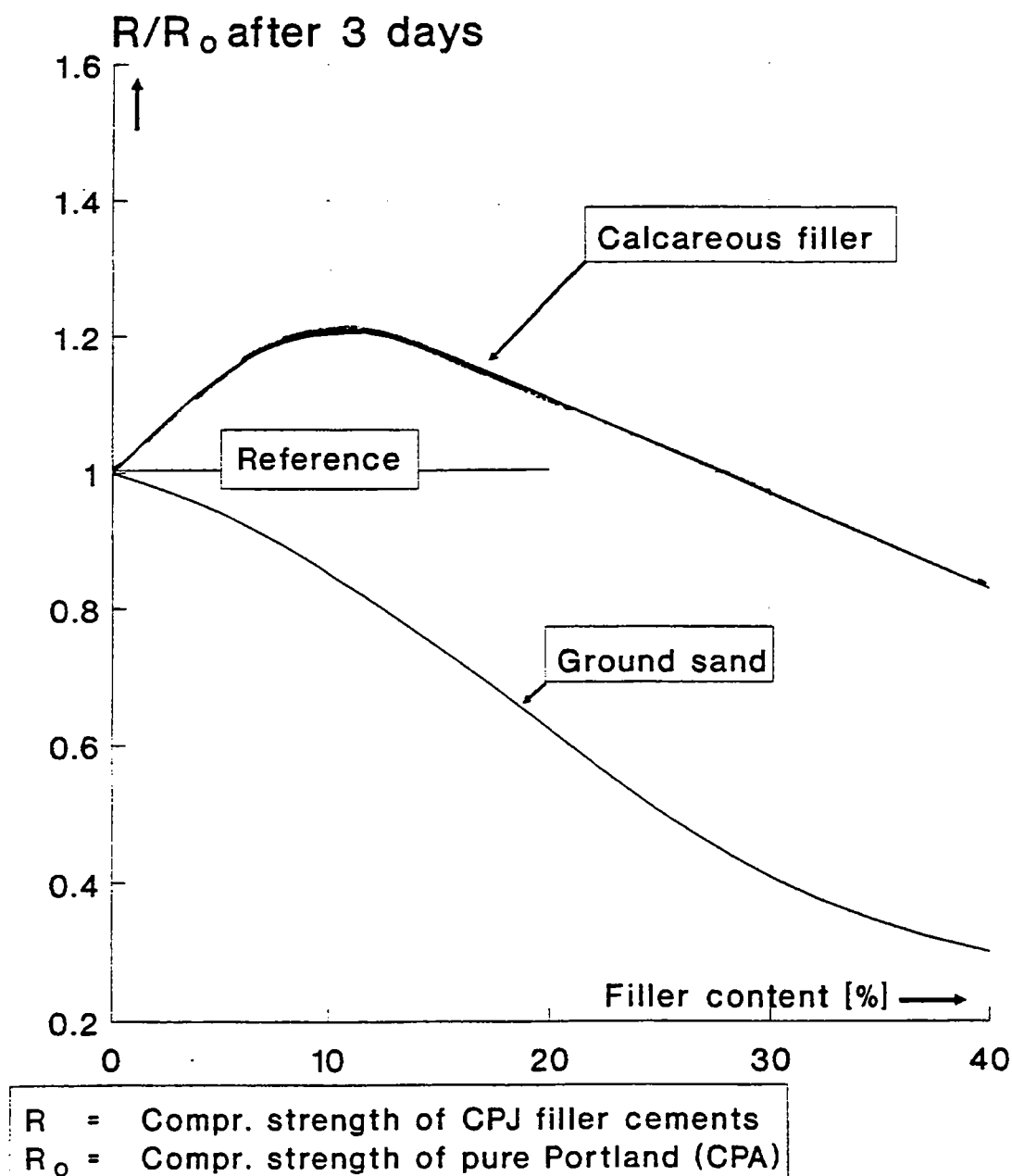
Table 16 Quality Characteristics of Industrially Produced Portland Limestone Cements

Origin		France	Germany
Limestone content	[%]	27.5	19.0
Fineness	[cm ² /g]	5150	4960
water requirement	[%]	27.7	25.7
Init. setting	[min.]	95	95
<u>ISO mortar</u>	[N/mm ²]		
	1 d	16.5	13.0
	2 d	26.1	22.9
	7 d	38.5	41.0
	28 d	48.0	49.7

7.4 Concrete Properties

- ◆ Water requirement of standard concrete is influenced by both the nature of the limestone and the filler content in a non-linear way. However, the workability is often improved by addition of limestone filler as is the response to addition of superplasticizers/water reducers in concrete.
- ◆ Early strength development is usually not affected by the limestone content and the somewhat lower w/c ratio compensates for lower late strength.
- ◆ As long as the limestone meets the requirements of the standards, the susceptibility of mortar and concrete to frost and frost/thaw is only directly connected to the quality of concrete (the use of air-entraining agent is required).

Fig. 16 Influence of Calcareous Filler in Limestone Cement on Early Strength



7.5 Masonry Cements

Masonry cements can be considered as a special type of blended limestone cements; they actually contain 40 to 75% limestone and suitable chemical admixtures such as air-entraining agent and/or plasticizer.

Characteristics of masonry cements are reported in the chapter on Special Cements, to summarize it here, the choice of limestone (and other minor constituents like kiln dust, fly ash, slag) must be focussed on the obtainment of the following properties

- good adhesion, bond strength
- good cohesion and plasticity
- high water retention
- no segregation
- air-entrainment (15 to 20% vol) without foam formation
- improved impermeability.

7.6 Conclusion

The experience with manufacturing and utilization of limestone blended cements has shown that they exhibit favorable characteristics compared to pure Portland cements or other types of blended cements.

Limestone fillerized cements enable the cement industry to continue offering a standard high quality product at a favorable price, despite potential shortage of conventional additions such as slag and pozzolan.

8. TRENDS OF PRODUCTION AND MARKETING COMPOSITE CEMENTS

Rather than talking about cements, it will be necessary in the next years to consider binding agents and concrete mixes, in which Portland cement clinker will still be the principal active ingredient, but whose quantity should have to be drastically reduced for evident problems of environment awareness and reduction of emissions (CO, SO, NO, etc.).

Already today, concretes are being produced in which the clinker represents only 40% (and in some cases less than 20%) of the binding agent, the rest of the constituents such as fly ash, silica fume, ground slag, limestone filler, etc. being added directly at the concrete batching plant.

If we want to maintain the same quality of concrete and assure the future of our industry, we must increase drastically the proportion of additions in cement and master the production of binders with a maximum content of clinker substitutes. The possibilities for substitution are numerous and may be divided into three principal categories:

- ♦ Hydraulic materials for which the level of the average substitution of clinker will be in the order of 50% and may achieve 90% in the case of slag.
- ♦ Natural pozzolanic materials which will be able to substitute up to 30 to 40% of the clinker, but which require a definite proportion of CaO as activator.
- ♦ Artificial hydraulic and/or pozzolanic materials for which the level of substitution will be of the same order as of the two former categories, depending on their hydraulic and/or pozzolanic properties.

The real degree of replacement for these types of substitute materials will vary as a function of their individual reactivity. They can be mixed with other types of possible additions (triple blends or multi-blends or 'cocktail' cements), the clinker (or the activator) proportion depending on the quantity of CaO needed for the activation of the additions.

The reduction of the quantity of slag available for cement production on the market as well as the necessity of reducing the emissions, will require the production of thermally activated substitutes for clinker.

9. LITERATURE REFERENCES

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